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Ceramic materials for use in insert-casting and processes
for producing the same

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Chemical Abstract-"Ceramic Material for Use as a Port Liner to be Insert Cast-Has Aluminum Titanate as Major Crystalline Phase", J63-236,759 (10/3/88) (Japan Patent Pub.).

Chemical Abstract-"Aluminum Titanate Honeycomb Ceramic-for Treating Automobile Exhaust Gases" J56-89844 (7/21/81) (Japan Patent Public.).

Chemical Abstracts-"Aluminum Titanate Honeycomb, Useful as Catalyst Carrier-Comprising Aluminum Titanate, at least 1 of Lantharum, Cerium, and Yttrium Oxide and Opt. Ferric Oxide", Japanese Patent Public. 56-92,164-(7/25/81).

Japanese Patent Abstract-56-89844 "Ceramic Honeycomb and Its Production" 7/21/81 (same as Chem. Abstract 2).

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CORE TERMS: phase, crystal, aluminum, cracked, particle, glass, titanate, kgf, source material, cooling-heating, ceramic, strain, oxide, ceramic material, cycle, rare earth element, modulus, insert-casting, rupture, cooling, volume, sintered, bending, firing, composition, crack, heat, porosity, thermal, crystalline

ABST:

A ceramic material for use in insert-casting, which contains not less than 65% by volume of aluminum titanate as a crystalline phase. The average particle diameter of crystals of the aluminum titanate is not less than 10 μ m, and not more than 20% by volume of a glass phase containing a rare earth element in an amount of 0.5 to 16% by weight when calculated in the form of an oxide is contained. Young's modulus is 50 to 2,000 kgf/mm². A process for producing the same is also disclosed, which includes the steps of preparing a powder by mixing a material, as an Al₂O₃ source material, containing not more than 96% by weight of Al₂O₃ and having an average particle size of not less than 3 μ m, a material having an average particle diameter of not more than 3 μ m as a TiO₂ source material, and a given rare earth element in an amount of 1.8% by weight when calculated in the form of an oxide, shaping the powder, and drying and firing the shaped body. The ceramic material has an actual break strain of not less than 6×10^{-3} . The process for producing such a ceramic material includes a step of cooling the shaped body at a rate of at least not less than 500° C./hr in a temperature range not less than 200° C. during and/or after the firing.

NO-OF-CLAIMS: 15

EXMPL-CLAIM: <=10> 1

NO-OF-FIGURES: 15

NO-DRWNG-PP: 10

SUM:

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to ceramic materials for use in enclosing a hollow tubular ceramic material by insert-casting with a melt of a metal such as aluminum or cast iron. Particularly, the invention relates to heat-insulating ceramic materials for use in insert-casting as port liners, exhaust manifold liners, piston cavities, cylinder top plates, etc. in gasoline engines, diesel engines and the like. The invention also relates to processes for producing such ceramic materials.

2. Related Art Statement

Recently, environmental pollution caused by with automobile exhaust gases has become a serious social problem, and methods for removing poisonous materials from the automobile exhaust gases with use of catalysts are mainly employed. Reduction in use amounts of noble metals such as Pt, Rh, etc. used as catalysts therefor results in a problem from the stand point of natural resources and costs. Further, four valve engines, which have recently increasingly been employed, pose a problem in that a catalytic purification performance is reduced by reduction in temperatures of exhaust gases.

As one method for solving the above problems, Japanese Patent Application Laid-open No. 63-236,759 proposes that the inner surface of an exhaust port or an exhaust port liner is lined with a port liner made of a ceramic material having a low Young's modulus so that the temperature of exhaust gases may be increased by its heat insulating property. Further, Japanese Patent Publication No. 57-3,629 and Japanese Patent Application Laid-open No. 56-92,164 disclose the addition of a rare earth element to aluminum titanate as also intended in the present invention.

However, there are problems that the materials disclosed in Japanese Patent Application Laid-open No. 63-236,759 suffer deterioration in strength due to a cooling-heating cycle owing to changes in temperatures of the exhaust gases when in use, and that the materials are broken.

In the inventions of both Japanese Patent Publication No. 57-3,629 and Japanese Patent Application Laid-open No. 56-92,164, dense sintered bodies having a low thermal expansion are obtained by adding a given amount of an oxide of Y, La and/or Ce to aluminum titanate. However, Young's modulus of all these sintered bodies are high, and they cannot be used for materials in insert-casting.

As the ceramic materials used for increasing the temperature by their heat insulating property, those having lower Young's modulus are preferred, because they can mitigate great compression stresses occurring through shrinkage of a molten metal during insert-casting of liners. NGK Insulators, Ltd. have formerly developed ceramic materials for use in insert-casting, in which not less than 65% by volume of aluminum titanate is contained as a crystalline phase, and proposed them in Japanese Patent Application Laid-open No. 63-236,759.

However, succeeding researches revealed that although the above materials had

the Young's modulus E falling in the range from 50 to 2,000 kgf/mm², some of them were broken upon insert-casting, while others were not. Therefore, stable insert-castability cannot be assured, which poses a practical problem.

The present invention is to solve the conventional problems mentioned above, and has been accomplished to provide practical ceramic materials suitable for insert-casting, which have excellent heat resistance, thermal shock resistance and heat insulation, are free from the occurrence of cracks owing to compression forces generated on insert-casting, and have durability in cooling-heating cycles during use. The invention also provides processes for producing such ceramic materials.

SUMMARY OF THE INVENTION

The ceramic materials for use in insert-casting according to a first aspect of the present invention are characterized in that 65% by volume of aluminum titanate is contained as a crystalline phase, not less than the average particle diameter of crystals is not less than 10 μ m, that an amount of a glass phase containing a rare earth element in an amount of 0.5 to 16% by weight calculated as an oxide is not more than 20% by volume, and that a Young's modulus is 50 to 2,000 kgf/mm².

Further, the process for producing the ceramic materials for use in insert casting according to the present invention comprises the steps of: preparing a powder having a given composition consisting essentially of a starting material containing not more than 96% by weight of Al₂O₃ and having an average particle diameter of not more than 3 μ m as an Al₂O₃ source material, a starting material having an average particle diameter of 3 μ m as a TiO₂ source material, and a rare earth element in an amount of not more than 1.8% by weight when calculated in the form of an oxide; shaping the powder; and drying and firing the shaped body.

A second aspect of the present invention has been accomplished based on the following recognition:

The present inventors have repeated studies to accomplish the object of the present invention, and discovered that although the conventional Young's modulus is determined based on a correlation formula between the strain and the stress in the elastic region of the material, with respect to a ceramic material for use in insert-casting as in the present invention, a deflected amount of the materials, which results in actual breakage of the material, has an important meaning in the judgment as to whether cracks will occur or not, and that physical properties of the material should be evaluated based on a below-mentioned actual rupture strain calculated based on the deflected amount.

The ceramic materials according to the second aspect of the present invention are characterized in that not less than 65% by volume of aluminum titanate is contained as a crystalline phase, that the average particle diameter of the crystals of aluminum titanate is not less than 10 μ m, and that the actual rupture strain is not less than 6×10^{-3} .

The actual rupture strain used herein means a nondimensional quantity defined by the following equation: [See equation in original]

Although Young's modulus is generally a ratio of stress/strain in an elastic

region of the material, "Young's modulus at break" used herein means an imaginary Young's modulus obtained by the deflective amount of the material until the material is broken during the measurement of the four point bending strength.

A third aspect of the present invention, which is an improvement of the second aspect of the present invention, is characterized in that not less than 65% by volume of aluminum titanate is contained as a crystalline phase, that an average particle diameter of the crystals of aluminum titanate is not less than 10 μ m, that a glass phase containing a rare earth element in an amount of 0.5 to 16% by weight when calculated in the form of an oxide is not more than 17% by volume, and that the actual rupture strain is not less than 6×10^{-3} .

The process for producing the ceramic materials for use in insert-casting according to the second aspect of the present invention comprises the steps of: preparing a powder having a given composition consisting essentially of a starting material containing not more than 96% by weight of Al_2O_3 and having an average particle diameter of not less than 3 μ m as an Al_2O_3 source material, and a material having an average particle diameter of not more than 3 μ m as a TiO_2 source material: shaping a powder: firing the shaped body: and cooling the body at a speed of not less than 500°C./hr from a temperature not less than 200°C. during the firing and/or after the firing.

The process for producing the ceramic materials for use in insert-casting according to the third aspect of the present invention comprises the steps of: preparing a powder having a given composition consisting essentially of a starting material containing not more than 96% by weight of Al_2O_3 and having an average particle diameter of not less than 3 μ m as an Al_2O_3 source material, a starting material having an average particle diameter of not more than 3 μ m as a TiO_2 source material, and a rare earth element in an amount of not more than 1.8% by weight when calculated in the form of an oxide: shaping the powder, drying and firing the shaped body, and cooling the body at a speed of not less than 500°C./hr from a temperature not less than 200°C. during the firing and/or after the firing.

Since coefficients of thermal expansion of a- and b-axes of the aluminum titanate crystal are positive, while that of a c-axis is negative. Further, differences among them are great. Thus, strain occurs in the grain boundaries owing to changes in temperatures such as cooling-heating cycles. In conventional materials constituted by fine crystals, such a strain does not cause into a great problem. On the other hand, particularly in the case of Young's modulus-reduced ceramic materials for use in insert-casting, in which crystals of aluminum titanate are grown up to not less than 10 μ m on the average, it was found out that the above strain becomes so large that the gap between the grains widens to lower strength.

To the contrary, the present inventors have found that when a very small amount of at least one rare earth element such as Y, Ce or La is added, reduction in strength by the cooling-heating cycles can be prevented. This is considered that the added rare earth element collects at the intergranular glass phase to increase strength of the glass phase and bonding forces between the glass phase and the aluminum titanate crystals.

That is, the present invention has been accomplished on the basis of the above-mentioned ceramic materials having the structure which has aluminum

titanate having a given average crystalline particle diameter as a main crystalline phase and in which the glass phase containing a given amount of the rare earth element is present in the grain boundaries of the aluminum titanate crystals can attain low Young's modulus aimed at by the present invention and durability in cooling-heating cycles.

As a method for producing the ceramic material having the above crystalline structure, the ceramic material for use in insert-casting can be obtained, by using a coarse Al_2O_3 source material having a low purity, a fine TiO_2 source material, and a given amount of a rare earth element, in which not less than 65% by volume of aluminum titanate is contained as a favorable crystalline phase of the above material, the average particle diameter of the crystals is not less than 10 μm , Young's modulus is 50 to 2,000 kgf/mm^2 , compression strength is 5 to 40 kgf/mm^2 , and porosity is 5 to 35%.

These and other objects, features and advantages of the invention will be appreciated upon reading of the following description of the invention when taken in conjunction with the attached drawings, with the understanding that some modifications, variations and changes of the same could be made by the skilled person in the art to which the invention pertains without departing from the spirit of the invention or the scope of claims appended hereto.

DRWDESC:

BRIEF DESCRIPTION OF THE ATTACHED DRAWINGS

For a better understanding of the invention, reference is made to the attached drawings, wherein:

FIG. 1 is a perspective view of a port liner for use in a four valve engine;

FIG. 2 is a sectional view of a port liner inserted in an engine head by casting;

FIG. 3 is a sectional view of an exhaust manifold liner after insert-casting;

FIG. 4 is a graph illustrating a cooling-heating cycle for evaluation in the present invention;

FIGS. 5a and 5b are SEM photographs showing the structures of crystals in a fired body according to the present invention before and after the cooling-heating cycle, respectively;

FIGS. 6A and 6B are SEM photographs showing the structures of a fired body in Comparative Examples before and after the cooling-heating cycle, respectively;

FIG. 7 is a graph showing an example of schedules of rapidly cooling conditions;

FIGS. 8a and 8b are a vertical cross-sectional view and a horizontal sectional view of a test piece used in an insert-casting test, respectively;

FIGS. 9a and 9b are a graph showing changes in actual rupture strain when a rapidly cooling-starting temperature was changed in the rapidly cooling treating conditions, and a graph showing changes in actual rupture strain when a cooling rate was varied in the rapidly cooling conditions, respectively; and

FIGS. 10a and 10b are an SEM photograph of the structure of crystals in a fired body rapidly cooled after firing, and an SEM photograph showing the structure of crystals in a fired body as a comparative example, respectively. DETDESC:

DETAILED DESCRIPTION OF THE INVENTION

Reasons for the limitations in the ceramic materials according to the present invention and their preferable ranges are as follows:

The reasons why the amount of aluminum titanate and the average particle diameter of the crystals of the aluminum titanate are limited to not less than 65% by volume and not less than 10 μm , respectively, are that the amount or the average particle diameter are less than 65% by volume or less than 10 μm , respectively, Young's modulus exceeds 2,000 kgf/mm^2 so that cracks occur on insert-casting.

Further, if the amount of the glass phase is more than 20% by volume, Young's modulus exceeds 2,000 kgf/mm^2 . Thus, the amount of the glass phase is limited to not more than 20%.

In addition, if the amount of the rare earth element in the glass phase is less than 0.5% by weight when calculated in the form of the oxide, the reduction rate in the four point bending strength in the cooling-heating cycle is more than 10%. If the rare earth element exceeds 16% by weight, Young's modulus becomes more than 2,000 kgf/mm^2 . Thus, the content of the rare earth element in the glass phase is limited to 0.5 to 16% by weight when calculated in the form of the oxide.

Reason for the preferable ranges in the present invention are as follows:

If the compression strength is less than 5 kgf/mm^2 and/or if the four point bending strength is less than 0.2 kgf/mm^2 , the ceramic material may be deformed on insert-casting, so that handling problems rise. If the compression strength is more than 40 kgf/mm^2 or if the four point bending strength is more than 2.0 kgf/mm^2 , Young's modulus may exceed 2,000 kgf/mm^2 . Further, if the porosity is less than 5%, a sufficient heat insulating effect cannot be obtained. If the porosity is more than 35%, Young's modulus may fall outside the numerical range in the present invention. It is most preferable that the Young's modulus is set particularly at 50 to 200 kgf/mm^2 . If the rare earth element in the glass phase exceeds 10% by weight when calculated in the form of the oxide, Young's modulus becomes greater than 200 kgf/mm^2 . In addition, it is preferable that the composition of the ceramic material consists essentially of 40 to 65% by weight of Al_2O_3 and 30 to 60% by weight of TiO_2 . The reason for this is that if the composition falls outside the above composition, the crystal amount of the aluminum titanate is difficult to exceed 65% by volume. The reason why at least one kind of SiO_2 , MgO and Fe_2O_3 is preferably in a total amount of not more than 10% is that if it exceeds 10% by weight, the crystal amount of the aluminum titanate is also difficult to exceed not less than 65% by volume, and the crystalline particle diameter may not be 10 μm or more. Furthermore, when the ceramic material according to the present invention possesses the coefficient of thermal expansion of not more than 2.0×10^{-6} (400 to 800°C.) and a heat conductivity of 0.8×10^{-3} to 5.0×10^{-3} $\text{cal/cm} \cdot \text{sec} \cdot ^\circ\text{C}$.

C., the material is suitable for port liners to be brought into direct contact with exhaust gases at high temperatures.

Next, reasons for the limitations in the Al_2O_3 source material and the TiO_2 source material in the producing process according to the first aspect of the present invention are as follows:

If the Al_2O_3 source material has the purity of more than 96% and the average particle diameter of more than 3 μm , the amount of the unreacted portion increases due to low reactivity of the Al_2O_3 source material so that Young's modulus becomes higher than 2,000 kgf/mm^2 because of insufficient growth of microcracks and that cracking of the ceramic material is feared on insert-casting with aluminum. Furthermore, if the average particle diameter of the Al_2O_3 source material is less than 3 μm , the average particle diameter of aluminum titanate is reduced to less than 10 μm irrespective of the purity of the Al_2O_3 , so that Young's modulus becomes higher than 2,000 kgf/mm^2 . Moreover, if the content of impurities contained in the Al_2O_3 source material is more than 20% by weight of SiO_2 , more than 20% by weight of Fe_2O_3 , or more than 20% by weight of $\text{SiO}_2 + \text{Fe}_2\text{O}_3$ in total, it may be that the amount of the aluminum titanate is less than 65% by volume and that the average crystal particle diameter is not less than 10 μm . From the above, the Al_2O_3 source material must have the purity of not more than 96% by weight and the average particle diameter of not less than 3 μm . The amount of the impurities is preferably 0 to 20% by weight of SiO_2 , 0 to 20% by weight of Fe_2O_3 , or 0 to 20% by weight of $\text{SiO}_2 + \text{Fe}_2\text{O}_3$ in total.

If the average particle diameter of the TiO_2 source material is more than 3 μm , the amount of the unreacted portion increases, so that Young's modulus exceeds 2,000 kgf/mm^2 . Thus, it is feared that the material will crack during insert-casting with aluminum. Therefore, the TiO_2 source material has the average particle diameter of not more than 3 μm .

When the rare earth element such as Y, La or Ce is added in an amount of not more than 1.8% by weight, Young's modulus can be controlled to not more than 2,000 kgf/mm^2 . If it is added in an amount less than 0.3% by weight, Young's modulus can be controlled to not more than 200 kgf/mm^2 .

In order to produce the ceramic materials according to the first aspect of the present invention, materials are selected from alumina, calcined bauxite, purified rutile, crude rutile, anatase type titanium, ilmenite, ferrite red iron oxide, electrofused magnesium, magnesite, electrofused spinel, kaoline, quartz, electrofused silica, specific rare earth elements, etc. to give a chemical composition consisting essentially of 40 to 65% by weight of Al_2O_3 , 30 to 60% by weight of TiO_2 , and not more than 10% by weight of at least one kind of SiO_2 , MgO and Fe_2O_3 in total.

At that time, it is necessary that a starting material containing less than 96% purity by weight of Al_2O_3 and the average particle diameter of not less than 3 μm as the Al_2O_3 source material is mixed with a material having the average particle diameter of not more than 3 μm as the TiO_2 source material.

Further, the rare earth element may be added in the form of a nitrate, an oxide or any other compound. In order to obtain an intended effect with a very small addition amount of the rare earth element, it is preferable to uniformly

disperse fine particles of the material thereof.

0.1 to 1.0% by weight of a deflocculant selected from water glass, ammonium polycarbonates, amines, sodium pyrophosphates, or the like is added to the mixture, to which 1.0 to 5.0% by weight of a binder selected from PVA, MC, CMC, acrylates or the like is added. The resulting mixture is sufficiently mixed and stirred by means of a trommel, a pot mill or the like together with 15 to 40% by weight of water to prepare a slurry having a viscosity of 200 to 1,000 cp. The slurry is shaped in a cylindrical form or in the form of a port liner by casting, which is dried and fired. As a result, the aluminum titanate sintered body can be obtained, which has excellent heat resistance, thermal shock resistance, heat insulation and durability in cooling-heating cycles and which contains not less than 65% by weight of aluminum titanate as a crystalline phase and not more than 20% by weight of the glass phase involving 0.5 to 16% by weight of the rare earth element when calculated in the form of the oxide. One or more kinds of rutile, corundum and mullite may be contained as other crystalline phases. According to the present invention, the crystals of aluminum titanate are sufficiently grown to not less than 10 μ m by setting the firing conditions to, for instance, 1,450° to 1,650° C., preferably 1,500° to 1,600° C., for 1 to 16 hours. By so doing, the ceramic material can acquire physical properties of Young's modulus of 50 to 2,000 kgf/mm², preferably compression strength of 5 to 40 kgf/mm², four point bending strength of 0.2 to 2.0 kgf/mm², and porosity of 5 to 35%. Since the ceramic materials having such a low Young's modulus can shrink together with a metallic material when the cast metallic material shrinks, no cracks occur due to concentration of stress particularly in the case of such a complicated shape as to break a conventional, high strength, high Young's modulus ceramic due to concentration of stresses.

Therefore, the ceramic materials according to the present invention can favorably be applied to, as a matter of course, conventional cylindrical port liners as well as a port liner 3 having a complicated shape shown in FIG. 1 or 2 and a port liner for an exhaust manifold as shown in FIG. 3. In these figures, two ports 2 are provided on a cylinder side of a four valve engine, and a single exhaust opening 1 is provided in an exhaust manifold side. Heat conductivity is lowered by the cracks in the sintered body, so that a sufficient heat insulating effect can be obtained even when the porosity is relatively small.

Since aluminum titanate has a melting point of not less than 1,700° C., no particular limitation is posed upon metals to be cast. Gray cast iron, nodular graphite cast iron, white cast iron, aluminum alloy, copper alloy, magnesium alloy, and zinc alloy may be used for insert casting.

Further, the intergranular glass phase is firmly bonded to aluminum titanate by making a very small amount of a rare earth element present in the glass phase, so that the ceramic material having durability in the cooling-heating cycle can be obtained without deteriorating low Young's modulus favorable for insert-casting.

Next, Examples of the first aspect of the present invention will be explained below.

EXPERIMENT 1

By using an Al₂O₃ source material shown in Table 1 and a TiO₂ source material shown in Table 2 as main components, a raw material was formulated to give each

of compositions in Test Run Nos. 1-35 shown in Table 3, and cast into a mold, thereby preparing elliptical section test pieces having a thickness of 3 mm, a main axis of 64 mm and a minor axis of 36 mm. Each test piece was fired under conditions given in Table 3, and various physical properties were measured with respect to thus obtained fired bodies.

Next, after molding sand is charged into each fired body, it was enclosed with aluminum by casting to prepare a metal-ceramic composite body having an aluminum thickness of 7 mm. After the molding sand was removed, it was checked whether cracks occurred in the test piece or not. Results are shown in Table 3.

In a cooling-heating cycle test of Table 1, the test piece was repeatedly subjected to a cooling-heating cycle of keeping it at room temperature for 10 minutes and 900°C. for 20 minutes at 50 times as shown in FIG. 4. FIG. 4 gives a schedule and the temperature of the cooling-heating cycle. A reduction rate of the four point bending strength of the test piece between before and after the cooling-heating cycle test was measured. Amounts of aluminum titanate and a glass phase were determined as % by volume based on their area-occupying rates in an SEM photograph. Further, an amount of a rare earth element in the glass phase was measured by an EDX analysis by means of a transmission electron microscope.

In order to facilitate observation of changes in the cooling-heating cycle with respect to the materials according to the present invention and as Comparative Examples, FIGS. 5a, 5b, 6a and 6b are microphotographs of sintered body, and sintered body having undergone the above cooling-heating by 600 times. That is, FIGS. 5a and 5b show the crystalline structures of the fired body according to the present invention before and after the cooling-heating cycles, respectively. FIGS. 6a and 6b show the crystalline structures of the fired body of Comparative Example before and after the cooling-heating cycle, respectively. From FIGS. 5a, 5b, 6a and 6b, it is seen that the gap is widened by the cooling-heating cycle in the ceramic material of Comparative Example, but that no conspicuous difference is recognized between before and after the cooling-heating cycle in the ceramic materials according to the present invention.

TABLE 1

		A-1	A-2	A-3	A-4	A-5
Chemical analysis value (wt %)	SiO ₂	0.9	2.1	2.7	2.7	2.4
	Al ₂ O ₃	98.1	96.0	94.8	95.1	95.3
	Fe ₂ O ₃	0.1	0.4	0.5	0.4	0.4
	TiO ₂	0.6	1.3	1.8	1.6	1.7
	Others	0.3	0.2	0.2	0.2	0.2
Average particle diameter (μm)		12.9	13.1	9.8	3.0	1.4

TABLE 2

		T-1	T-2	T-3
Chemical analysis	SiO ₂	0.0	0.0	0.0
	Al ₂ O ₃	0.0	0.0	0.0

value	Fe ₂ O ₃	0.0	0.0	0.0
(wt %)	TiO ₂	99.6	99.4	99.5
*	Others	0.4	0.6	0.5
Average particle diameter (μ m)		5.8	3.0	0.7

TABLE 3 (a)

Run No.	1	2	3	4
Al ₂ O ₃ source material	A-3	A-3	A-3	A-3
TiO ₂ source material	T-3	T-3	T-3	T-3
Composition				
Al ₂ O ₃ (wt %)	43.3	43.3	53.8	53.8
TiO ₂	53.4	53.4	42.2	42.2
SiO ₂	3.3	3.3	3.0	3.0
MgO	-	-	-	-
Fe ₂ O ₃	-	-	1.0	1.0
Oxide of rare earth element	-	0.25	-	0.05
	*	(Y ₂ O ₃)	*	(CeO ₂)
Firing temperature (°C.)	1550	1550	1550	1550
Young's modulus (kgf/mm ²)	1330	1410	120	120
Compression strength (kgf/mm ²)	23	23	11	10
Four point bending strength (kgf/mm ²)	1.1	1.2	0.4	0.4
Porosity (%)	5.8	5.9	8.5	8.7
AT crystal average particle size (μ m)	16	17	20	20
AT crystal amount (%)	84	83	92	92
Glass phase amount (%)	9	9	8	8
Amount of rare earth element oxide in glass phase (%)	-	13.5	-	0.5
Coefficient of thermal expansion ($\times 10^{-6}$ /°C.)	- 1.0	- 1.3	- 1.4	- 1.5
Heat conductivity ($\times 10^{-3}$ cal/cm x s x °C.)	-	1.7	1.4	-
Crystal phase other than AT	rutile	rutile	-	-
Occurrence of cracks	not cracked	not cracked	not cracked	not cracked
Reduction rate in four point bending strength in cooling-heating cycle (%)	19	- 1	23	9
Remarks	Comparative Example	Example *	Comparative Example	Example

TABLE 3 (b)

Run No.	5	6	7	8
Al ₂ O ₃ source material	A-3	A-3	A-3	A-3
TiO ₂ source material	T-3	T-3	T-3	T-3
Composition				
Al ₂ O ₃ (wt %)	53.8	53.8	53.8	53.8
TiO ₂	42.2	42.2	42.2	42.2
SiO ₂	3.0	3.0	3.0	3.0
MgO	-	-	-	-
Fe ₂ O ₃	1.0	1.0	1.0	1.0
Oxide of rare earth element	0.25 (CeO ₂)	1.0 (CeO ₂)	1.5 (CeO ₂)	2.5 (CeO ₂)
Firing temperature (°C.)	1550	1550	1550	1550
Young's modulus (kgf/mm ²)	130	340	1420	2310
Compression strength (kgf/mm ²)	11	12	35	44
Four point bending strength (kgf/mm ²)	0.4	0.6	1.4	2.2
Porosity (%)	8.8	8.3	7.4	6.1
AT crystal average particle size (μm)	19	15	12	9
AT crystal amount (%)	92	91	91	90
Glass phase amount (%)	8	9	9	10
Amount of rare earth element oxide in glass phase (%)	2.8	10.6	16.0	25.3
Coefficient of thermal expansion (× 10 ⁻⁶ /°C.)	- 1.7	- 1.8	- 1.7	- 1.8
Heat conductivity (× 10 ⁻³ cal/cm × s × °C.)	1.4	-	-	-
Crystal phase other than AT	-	-	-	-
Occurrence of cracks	not cracked	not cracked	not cracked	cracked
Reduction rate in four point bending strength in cooling-heating cycle (%)	0	1	- 1	0
Remarks			Example *	Comparative Example

TABLE 3 (c)

Run No.	9	10	11	12
Al ₂ O ₃ source material	A-3	A-3	A-3	A-3
TiO ₂ source material	T-3	T-3	T-3	T-3
Composition				
Al ₂ O ₃	53.8	53.8	53.8	44.0

(wt %)	TiO ₂	42.2	42.2	42.2	52.0
	SiO ₂	3.0	3.0	3.0	3.0
	MgO	-	-	-	-
	Fe ₂ O ₃	1.0	1.0	1.0	1.0
	Oxide of rare earth element	0.25	0.25	0.25	0.25
		(La ₂ O ₃)	(Y ₂ O ₃)	(Dy ₂ O ₃)	(CeO ₂)
Firing temperature (°C.)		1550	1550	1550	1600
Young's modulus (kgf/mm ²)		140	160	150	190
Compression strength (kgf/mm ²)		11	11	10	10
Four point bending strength (kgf/mm ²)		0.4	0.5	0.4	0.5
Porosity (%)		8.8	8.8	8.9	5.4
AT crystal average particle size (μm)		19	18	19	19
AT crystal amount (%)		92	92	92	75
Glass phase amount (%)		8	8	8	8
Amount of rare earth element oxide in glass phase (%)		2.8	2.9	2.8	2.8
Coefficient of thermal expansion (× 10 ⁻⁶ /°C.)		- 1.7	- 1.8	- 1.7	- 1.1
Heat conductivity (× 10 ⁻³ cal/cm × s × °C.)		1.3	1.4	1.4	-
Crystal phase other than AT		-	-	-	rutile
Occurrence of cracks		not cracked	not cracked	not cracked	not cracked
Reduction rate in four point bending strength in cooling-heating cycle (%)		2	- 1	1	2
Remarks					Example

TABLE 3(d)

Run No.	13	14	15	16
Al ₂ O ₃ source material	A-3	A-3	A-3	A-3
TiO ₂ source material	T-3	T-3	T-3	T-3
Composition (wt %)				
Al ₂ O ₃	49.0	53.8	55.7	62.9
TiO ₂	47.0	42.2	40.3	33.8
SiO ₂	3.0	3.0	3.0	3.3
MgO	-	-	-	-
Fe ₂ O ₃	1.0	1.0	1.0	-
Oxide of rare earth element	0.25	0.25	0.25	-
	(CeO ₂)	(CeO ₂)	(CeO ₂)	-
Firing temperature (°C.)	1600	1600	1600	1550

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Young's modulus (kgf/mm ²)	170	100	190	1890
Compression strength (kgf/mm ²)	10	9	11	37
Four point bending strength (kgf/mm ²)	0.5	0.4	0.5	1.7
Porosity (%)	6.8	7.4	11.4	12.4
AT crystal average particle size (μ m)	23	23	24	12
AT crystal amount (%)	83	92	86	80
Glass phase amount (%)	9	8	8	8
Amount of rare earth element oxide in glass phase (%)	2.6	2.5	2.9	-
Coefficient of thermal expansion ($\times 10^{-6}$ /oC.)	- 1.3	- 1.7	- 1.2	1.1
Heat conductivity ($\times 10^{-3}$ cal/cm x s x oC.)	1.2	-	-	-
Crystal phase other than AT	rutile *	- *	mullite *	corundum mullite
Occurrence of cracks	not cracked	not cracked	not cracked	not cracked
Reduction rate in four point bending strength in cooling-heating cycle (%)	2	2	3	12
Remarks			Example *	Comparative Example

TABLE 3(e)

Run No.	17	18	19	20
Al ₂ O ₃ source material	A-3	A-3	A-3	A-3
TiO ₂ source material	T-3	T-3	T-3	T-3
Composition (wt %)				
Al ₂ O ₃	62.9	54.2	54.2	54.2
TiO ₂	33.8	42.5	42.5	42.5
SiO ₂	3.3	1.1	1.1	1.1
MgO	-	1.1	1.1	1.1
Fe ₂ O ₃	-	1.1	1.1	1.1
Oxide of rare earth element	1.25 (Y ₂ O ₃)	- *	0.25 (CeO ₂)	0.5/0.5 (Y ₂ O ₃ /CeO ₂)
Firing temperature (oC.)	1550	1550	1550	1550
Young's modulus (kgf/mm ²)	2000	130	140	310
Compression strength (kgf/mm ²)	38	11	11	12
Four point bending strength (kgf/mm ²)	1.7	0.4	0.4	0.6
Porosity (%)	11.1	9.0	9.2	9.3
AT crystal average	12	19	18	18

particle size (μm)				
AT crystal amount (%)	79	93	93	93
Glass phase amount (%)	10	7	7	7
Amount of rare earth element oxide in glass phase (%)	12.1	-	2.7	13.9
Coefficient of thermal expansion ($\times 10^{-6}$ / $^{\circ}\text{C}$.)	0.9	- 1.5	- 1.7	- 1.8
Heat conductivity ($\times 10^{-3}$ cal/cm x s x $^{\circ}\text{C}$.)	1.5	1.2	1.3	1.2
Crystal phase other than AT	corundum mullite not	-	-	-
Occurrence of cracks	cracked	not cracked	not cracked	not cracked
Reduction rate in four point bending strength in cooling-heating cycle (%)	- 2	18	1	- 1
Remarks	Example *	Comparative Example		Example

TABLE 3(f)

Run No.	21	22	23	24
Al ₂ O ₃ source material	A-3	A-3	A-3	A-3
TiO ₂ source material	T-3	T-3	T-3	T-3
Composition (wt %)				
Al ₂ O ₃	54.3	54.3	55.5	54.2
TiO ₂	42.5	42.5	43.5	42.5
SiO ₂	1.6	1.6	1.0	3.3
MgO	1.6	-	-	-
Fe ₂ O ₃	-	1.6	-	-
Oxide of rare earth element	1.0 (Yb ₂ O ₃)	1.0 (Nd ₂ O ₃)	0.28 (Y ₂ O ₃)	0.28 (Y ₂ O ₃)
Firing temperature ($^{\circ}\text{C}$.)	1550	1550	1550	1550
Young's modulus (kgf/mm ²)	410	360	200	180
Compression strength (kgf/mm ²)	13	12	11	12
Four point bending strength (kgf/mm ²)	0.7	0.7	0.5	0.5
Porosity (%)	9.4	9.5	14.1	9.5
AT crystal average particle size (μm)	18	19	18	19
AT crystal amount (%)	91	91	97	92
Glass phase amount (%)	9	9	3	8
Amount of rare earth element oxide in glass	10.9	10.5	10.0	3.0

phase (%)				
Coefficient of thermal expansion ($\times 10^{-6}$ / $^{\circ}\text{C}$.)	- 1.7	- 1.6	- 1.8	- 1.7
Heat conductivity ($\times 10^{-3}$ cal/cm x s x $^{\circ}\text{C}$.)	-	-	-	-
Crystal phase other than AT	-	-	-	-
Occurrence of cracks	not cracked	not cracked	not cracked	not cracked
Reduction rate in four point bending strength in cooling-heating cycle (%)	- 1	0	- 1	- 1

Remarks

Example

		TABLE 3 (g)			
Run No.		25	26	27	28
Al ₂ O ₃ source material		A-3	A-3	A-1	A-2
TiO ₂ source material		T-3	T-3	T-3	T-3
Composition (wt %)	Al ₂ O ₃	51.6	50.4	54.3	54.3
	TiO ₂	40.4	39.6	42.5	42.5
	SiO ₂	8.0	10.0	1.6	1.6
	MgO	-	-	-	-
	Fe ₂ O ₃	-	-	1.6	1.6
	Oxide of rare earth element	1.8 (Y ₂ O ₃)	2.0 (Y ₂ O ₃)	1.0 (CeO ₂)	1.0 (CeO ₂)
Firing temperature ($^{\circ}\text{C}$.)		1550	1550	1500	1500
Young's modulus (kgf/mm ²)		1110	2030	2430	870
Compression strength (kgf/mm ²)		25	41	4	14
Four point bending strength (kgf/mm ²)		1.1	2.1	0.1	1.0
Porosity (%)		5.4	4.9	35.1	11.8
AT crystal average particle size (μm)		20	18	13*	18
AT crystal amount (%)		83	76	60	88
Glass phase amount (%)		17	24	7	9
Amount of rare earth element oxide in glass phase (%)		11.3	8.0	14.1	10.7
Coefficient of thermal expansion ($\times 10^{-6}$ / $^{\circ}\text{C}$.)		- 1.4	- 1.3	2.0	- 1.4
Heat conductivity ($\times 10^{-3}$ cal/cm x s x $^{\circ}\text{C}$.)		-	-	-	1.1
Crystal phase other than AT		-	-	rutile	corundum
		*	*	corundum	
Occurrence of cracks		not cracked	cracked	cracked	not cracked

Reduction rate in four point bending strength in cooling-heating cycle (%)	1	3	-	2
Remarks	Example	Comparative Example	Example	Example
TABLE 3 (h)				
Run No.	29	30	31	32
Al ₂ O ₃ source material	A-4	A-5	A-3	A-3
TiO ₂ source material	T-3	T-3	T-1	T-2
Composition (wt %)				
Al ₂ O ₃	54.3	54.3	54.3	54.3
TiO ₂	42.5	42.5	42.5	42.5
SiO ₂	1.6	1.6	1.6	1.6
MgO	-	-	-	-
Fe ₂ O ₃	1.6	1.6	1.6	1.6
Oxide of rare earth element	1.0 (CeO ₂)	1.0 (CeO ₂)	1.0 (CeO ₂)	1.0 (CeO ₂)
Firing temperature (°C.)	1500	1500	1500	1500
Young's modulus (kgf/mm ²)	1280	2850	2570	930
Compression strength (kgf/mm ²)	24	43	3	15
Four point bending strength (kgf/mm ²)	1.2	1.7	0.1	0.9
Porosity (%)	11.1	12.3	41.2	12.7
AT crystal average particle size (μm)	11	5	8	17
AT crystal amount (%)	94	92	59	86
Glass phase amount (%)	6	8	7	9
Amount of rare earth element oxide in glass phase (%)	15.9	12.1	13.8	11.1
Coefficient of thermal expansion (× 10 ⁻⁶ /°C.)	- 1.5	- 1.4	2.5	- 1.3
Heat conductivity (× 10 ⁻³ cal/cm × s × °C.)	1.1	-	-	1.0
Crystal phase other than AT	- *	- *	rutile corundum	rutile
Occurrence of cracks	not cracked	cracked	cracked	not cracked
Reduction rate in four point bending strength in cooling-heating cycle (%)	- 1	-	-	1
Remarks	Example	Comparative Example	Example	Example

Note: -

AT means aluminum titanate -

n*means that an unreacted portion exists in AT crystals. -

From results in Table 3, it is recognized that the ceramic materials according to the present invention are free from occurrence of cracks on insert-casting, and that they suffer fewer deterioration in the cooling-heating cycle test as compared with Comparative Examples.

As is clear from the foregoing explanation, according to the ceramic materials for use in insert-casting in the present invention and the production process thereof, by using coarse Al_2O_3 material having a low purity, fine TiO_2 source material and a rare earth element, it is possible to obtain the crystalline structure in which not less than 65% by volume of aluminum titanate is contained as the crystal phase, the average particle size of the crystals is not less than 10 μm , and 20% by volume of the glass phase containing the rare earth element in an amount of 0.5 to 16% by weight when calculated as an oxide is contained. As a result, the ceramic materials for use in insert-casting can be obtained, which have low Young's modulus, excellent heat resistance, thermal shock resistance and heat insulation and durability in the cooling-heating cycles, and are free from occurrence of cracks due to compression forces generated on the insert-casting.

Next, the second aspect of the present invention will be explained below in detail.

First, reasons for numerical limitations will be explained.

The reasons why the rate of aluminum titanate in the crystalline phase is limited to not less than 65% by volume and the average particle diameter is limited to not less than 10 μm are that if these requirements are not met, the actual rupture strain becomes less than 6×10^{-3} so that cracks occur on insert-casting. The reason why the actual rupture strain is limited to not less than 6×10^{-3} is that ceramic materials having the actual rupture strain of less than this value are likely to be cracked as shown in the below-mentioned experiment. Particularly, it is preferable to set the actual rupture strain to not less than 10×10^{-3} . Further, since the ceramic material contacts a molten metal at high temperature on insert-casting, it is preferable that the actual rupture strain is not less than 6×10^{-3} at high temperatures.

The third aspect of the present invention is to improve durability in the cooling-heating cycles by incorporating a rare earth element in the ceramic material. In this case, the glass phase is limited to 17% by volume, since if the content of the glass phase is more than 17% by volume, the actual rupture strain is less than 6×10^{-3} . Further, if the content of the rare earth element in the glass phase is less than 0.5% by weight when calculated in the form of the oxide, the reduction rate of the four point bending strength in the cooling-heating cycles exceeds 10%. To the contrary, if the content of the rare earth element is more than 16% by weight, the actual rupture strain becomes less than 6×10^{-3} . Thus, the oxide of the rare earth element in the glass phase is limited to the range from 0.5 to 16% by weight.

In the ceramic materials according to the second and third aspects of the present invention, sufficient heat-insulating effect cannot be obtained if the

porosity is less than 5%. To the contrary, if the porosity is more than 35%, the actual rupture strain may fall outside the range of the present invention. Further, it is preferable that the ceramic material has a composition consisting essentially of 40 to 65% by weight of Al_2O_3 and 30 to 60% by weight of TiO_2 . The reason for this is that if the composition does not meet this requirement, the amount of the crystals of aluminum titanate is difficult to exceed 65% by volume. The reason why at least one kind of SiO_2 , MgO , and Fe_2O_3 is contained in a total amount of not more than 10% by weight is that if the total amount is more than 10% by weight, it is difficult to attain the crystal amount of aluminum titanate of not less than 65% by volume, and the crystal diameter may be not more than 10 μm in some cases. The ceramic material according to the present invention has the coefficient of thermal expansion of not more than 2.0×10^{-6} (400 to 800 C.), and is suitable for port liners, etc. to be brought into direct contact with exhaust gases at high temperatures.

Next, reasons for the numerical limitations for the second and third aspects of the present invention are as follows:

If the purity of the Al_2O_3 source material is greater than 96% by weight and if the average particle size is more than 3 μm , much unreacted portion remains due to low reactivity of the Al_2O_3 source material, so that the actual rupture strain becomes less than 6×10^{-3} , and it is feared that the ceramic material cracks on insert-casting. Further, if the average particle diameter of the Al_2O_3 source material is less than 3 μm , the average particle diameter of aluminum titanate becomes less than 10 μm irrespective of the purity so that the actual rupture strain becomes less than 6×10^{-3} . Furthermore, if impurities contained in the Al_2O_3 source material are more than 20% by weight of SiO_2 , more than 20% by weight of Fe_2O_3 , or 20% by weight of $\text{SiO}_2 + \text{Fe}_2\text{O}_3$ in total, it may be that the content of the crystals of aluminum titanate is less than 65%, and that the average crystal particle diameter is less than 10 μm . From the above reasons, it is necessary that the Al_2O_3 source material has the purity of not more than 96%, and the average particle diameter of not less than 3 μm . The impurities are preferably 0 to 20% by weight of SiO_2 , 0 to 20% by weight of Fe_2O_3 , or 0 to 20% by weight of $\text{SiO}_2 + \text{Fe}_2\text{O}_3$ in total.

Further, when the average particle diameter of the TiO_2 source material is greater than 3 μm , the amount of the unreacted portion increases. Thus, the actual rupture strain becomes less than 6×10^{-3} . Consequently, there is a possibility that the ceramic material is cracked on insert-casting. Therefore, the average particle diameter of the TiO_2 source material must be not more than 3 μm .

In the production process for producing the ceramic material according to the third aspect of the present invention, the actual rupture strain of the ceramic material is increased by rapidly cooling it under the conditions that the maximum cooling rate is set at 500 C./hr in a temperature range from not less than 200 C. to 400 C. on the midway of the firing and/or after the firing. At that time, if the starting temperature is less than 200 C. or if the maximum cooling rate in the rapidly cooling treatment is less than 500 C./hr, the actual rupture strain cannot fully be increased. It is preferable that the starting temperature in the rapidly cooling treatment is set in a range from 350 to 1,100 C. and that the maximum cooling rate from the starting temperature of the rapidly cooling treatment is set to 2,000 C./hr. By so doing, the actual rupture strain can be increased to not less than 10×10^{-3} .

. If the starting temperature of the rapidly cooling treatment is more than 1,100° C., the increased rate of the actual rupture strain decreases. Consequently, aluminum titanate is decomposed, and there is a possibility that the ceramic material is broken on rapid cooling when the material is a product of a large size and complicated shape.

The reason why the addition amount of the rare earth element is limited to not more than 1.8% by weight in the production process for producing the ceramic material according to the third aspect of the present invention when calculated in the form of the oxide is to increase the actual rupture strain to not less than 6×10^{-3} .

In order to produce the ceramic materials according to the present invention, materials are selected from alumina, calcined bauxite, purified rutile, crude rutile, anatase type titanium, ilmenite, ferrite red iron oxide, electrofused magnesium, magnesite, electrofused, spinel, kaoline, quartz, electrofused silica, specific rare earth elements and the like to give a chemical composition consisting essentially of 40 to 65% by weight of Al_2O_3 , 30 to 60% by weight of TiO_2 , and not more than 10% by weight of at least one kind of SiO_2 , MgO and Fe_2O_3 in total. At that time, it is necessary that a starting material containing not more than 96% purity by weight of Al_2O_3 and the average particle diameter of not less than 3 μm as the Al_2O_3 source material is mixed with a material having the average particle diameter of not more than 3 μm as the TiO_2 source material. The rare earth element, which is added to improve durability in cooling-heating cycles, may be added in the form of a nitrate, an oxide or any other compound. In order to obtain an intended effect with a very small addition amount of the rare earth element, it is preferable to uniformly disperse a fine particles of the material. As the rare earth element, Y, La, Ce, Dy and Nd are economically preferred. La, Dy, and Nd have the same effect as that of Y.

0.1 to 1.0% by weight of a deflocculant selected from water glass, ammonium polycarboxylates, amines, sodium pyrophosphate and the like is added to the mixture, to which 1.0 to 5.0% of a binder selected from PVA, MC, CMC, acrylates and the like is added. The resulting mixture is sufficiently mixed and stirred by means of a trommel, a pot mill or the like together with 15 to 40% by weight of water to prepare a slurry having a viscosity of 200 to 1,000 cp. The slurry is shaped in a cylindrical form or in the form of a port liner by casting, which is dried and fired. As a result, the aluminum titanate sintered body can be obtained, which has excellent heat resistance, thermal shock resistance, heat insulation and durability in cooling-heating cycle and which contains not less than 65% by weight of aluminum titanate as the crystalline phase, and further not more than 17% by weight of a glass phase involving 0.5 to 16% by weight of the rare earth element, if added, when calculated in the form of the oxide. One or more kinds of rutile, corundum and mullite may be contained as other crystals.

According to the present invention, the crystals of aluminum titanate are sufficiently grown to the average particle diameter of not less than 10 μm contrary to the conventional common knowledge by setting the firing conditions to 1,450° to 1,650° C., preferably 1,500° to 1,600° C., for 1 to 16 hours. Further, when the ceramic material is to be cooled from not less than 200° C., preferably from not less than 350° C., to 40° C. during firing and/or after the firing, the material is rapidly cooled at the maximum cooling rate of not less

than 500° C./hr, preferably not less than 2,000° C./hr. The rapidly cooling is effected in the furnace by leaving the material in the furnace, blowing it with air, or throwing it into water. The above treatment may be effected by two or more times. By so doing, the material having the actual rupture strain of not less than 6×10^{-3} can be obtained. The reason why the actual rupture strain can be improved by the above-mentioned rapidly cooling is not completely solved at present. However, it is considered that the amount of very fine microcracks is increased in the aluminum titanate sintered body in such a range as to not almost lower strength.

The ceramic material having such a high actual rupture strain can be shrinked when the insert-cast metallic material contracts, and produces no cracks even when the material is shaped in such a complicated form as to break a conventional ceramic material having high strength and low actual rupture strain due to concentration of stress. Therefore, the ceramic materials according to the present invention are suitable for cylindrical port liners as well as a port liner 3 having a complicated shape in which two ports 2 and a single exhaust port 1 are provided on a cylinder side and on an exhaust manifold side of a four valve engine as shown in FIGS. 1 and 2, respectively, and an exhaust manifold liner 4 shown in FIG. 3. Microcracks in the sintered body lower heat conductivity, so that even a relatively small porosity can afford sufficient heat insulation.

Since aluminum titanate has a melting point of not less than 1,700° C., no limitation is posed upon a molten metal for insert-casting. Gray cast iron, nodular graphite cast iron, white cast iron, aluminum alloy, copper alloy, magnesium alloy, and zinc alloy may be employed for insert-casting.

By incorporating a very small amount of the rare earth element in the glass phase, the intergranular glass phase is firmly bonded to aluminum titanate so that the ceramic material having durability in cooling-heating cycle can be obtained without deteriorating high actual rupture strain as a favorable property for the insert casting.

Next, examples of the second and third aspects of the present invention will be explained below.

By using an Al₂O₃ source material shown in the above Table 1 and a TiO₂ source material shown in the above Table 2 as main ingredients, starting materials were formulated to give compositions in Test Run Nos. 33 to 45 in Table 4 and Test Run Nos. 46 to 60 shown in Table 5. Each of the materials was cast into a mold to form a test piece 5 having a bifurcated elliptical section shape of 4 mm thickness shown in FIG. 8. Each test piece was fired under conditions given in Tables 4 and 5, and various physical properties were measured with respect to the thus obtained fired bodies.

Next, after molding sand was charged into each of the sintered bodies, it was enclosed with aluminum by casting, thereby producing a metal-ceramic composite body having 7 mm thick aluminum. After the molding sand was removed, it was visually confirmed whether cracks occurred in the test piece or not. Results are shown in Tables 4 and 5.

In the cooling-heating cycle test of Table 5, the test piece was subjected to cooling-heating cycles shown in FIG. 4 in which the test piece was kept at room

temperature for 10 minutes and at 900°C. for 20 minutes by 50 times. Then, a reduction rate in the four point bending strength between before and after the test was measured. The amounts of aluminum titanate and the glass phase were calculated as % by volume by their area-occupying ratios in an SEM photograph. The content of the rare earth element in the glass phase was measured by an EDX analysis in a transmission electron microphotograph. In order to confirm changes in the rapid cooling treatment with respect to the materials according to the present invention and as comparative examples, FIGS. 10a and 10b show electron microphotographs of a sintered body and that having undergone the rapid cooling treatment, respectively. It is seen from FIGS. 10a and 10b that no great changes occurred in the crystalline structure by the rapid cooling treatment, and that strength was not changed by the rapid cooling. Further, FIG. 9a shows changes in the actual rupture strain when the cooling-starting temperature in the rapid cooling treatment was varied, and FIG. 9b shows changes in the actual rupture strain when the cooling rate in the rapidly cooling treatment was varied.

TABLE 4(a)

Run No.	33	34	35	36	37	38	39
Al ₂ O ₃ source material	A-3	A-3	A-3	A-3	A-3	A-2	A-4
TiO ₂ source material	T-3	T-3	T-3	T-3	T-3	T-3	T-3
Composit							
ion Al ₂ O ₃	44.0	53.8	53.8	54.2	62.9	54.3	54.3
(wt %) TiO ₂	52.0	42.2	42.2	42.5	33.8	42.5	42.5
SiO ₂	3.0	3.0	3.0	1.1	3.3	1.6	1.6
MgO	-	-	-	1.1	-	-	-
Fe ₂ O ₃	1.0	1.0	1.0	1.1	-	1.6	1.6
Firing temperature (°C.)	1600	1550	1600	1550	1550	1500	1500
Rapidly Starting temperature (°C.)	600	200	350	350	350	400	400
cooling (°C.)							
condi- Cooling rate (°C./HR)	10000	500	2000	2000	2000	1000	1000
tion							
Actual rupture strain (x 10 ⁻³)	17	8	18	17	12	9	9
Porosity (%)	5.2	7.0	7.2	9.1	11.5	11.8	10.9
AT crystal average particle size (μm)	20	11	24	18	13	18	10
AT crystal amount (%)	73	92	90	93	77	86	96
Coefficient of thermal expansion (x 10 ⁻⁶ /°C.)	- 1.1	- 1.5	- 1.6	- 1.8	0.8	- 1.0	- 1.3
Occurrence of cracks	not cracked	not cracked	not cracked	not cracked	not cracked	not cracked	not cracked
Remarks							Example

TABLE 4(b)

Run No.	40	41	42	43	44	45
Al ₂ O ₃ source material	A-3	A-3	A-3	A-1	A-5	A-3
TiO ₂ source material	T-2	T-2	T-3	T-3	T-3	T-1
Composition Al ₂ O ₃	54.3	53.8	62.9	54.3	54.3	54.3
(wt %) TiO ₂	42.5	42.2	33.8	42.5	42.5	42.5
SiO ₂	1.6	3.0	3.3	1.6	1.6	1.6
MgO	-	-	-	-	-	-
Fe ₂ O ₃	1.6	1.0	-	1.6	1.6	1.6
Firing temperature (°C.)	1500	1600	1550	1500	1500	1500
Rapidly Starting temperature (°C.)	400	400	600	400	400	400
cooling (°C.)						
condi- Cooling rate (°C./HR)	1000	500	100	1000	1000	1000
tion						
Actual rupture strain ($\times 10^{-3}$)	9	6	4	2	1	2
Porosity (%)	12.6	7.5	10.7	34.5	12.5	41.0
AT crystal average particle size (μ m)	17	21	12	14	6	9
AT crystal amount (%)	88	89	81	64	90	55
Coefficient of thermal expansion ($\times 10^{-6}$ /°C.)	- 1.1	- 1.4	1.2	2.0	- 1.4	2.1
Occurrence of cracks	not cracked	not cracked	cracked	cracked	cracked	cracked
Remarks	Example			Comparative Example		

TABLE 3

[See table in original]

TABLE 5(b)

Run No.	51	52	53	54	55
Al ₂ O ₃ source material	A-3	A-3	A-2	A-3	A-4
TiO ₂ source material	T-3	T-3	T-3	T-3	T-3
Composition Al ₂ O ₃	54.2	62.9	54.3	54.3	54.3
(wt %) TiO ₂	42.5	33.8	42.5	42.5	42.5
SiO ₂	1.1	3.3	1.6	1.6	1.6
MgO	1.1	-	-	-	-
Fe ₂ O ₃	1.1	-	1.6	1.6	1.6
Oxide of rare earth element	0.5/0.5 (Y ₂ O ₃ /CeO ₂)	1.25 (Y ₂ O ₃)	1.0 (CeO ₂)	1.0 (CeO ₂)	1.0 (CeO ₂)

Pat. No. 5066626, *

Firing temperature (oC.)	1550	1550	1500	1500	1500
Rapidly Starting cooling temperature condition (oC.)	350	350	400	400	400
Cooling rate (oC./HR)	2000	2000	1000	1000	1000
Actual rupture strain (x 10 ⁻³)	13	10	8	9	7
Porosity (%)	9.4	11.3	11.9	9.6	11.2
AT crystal average particle size (μ m)	18	12	18	19	10
AT crystal amount (%)	93	79	88	91	94
Glass phase amount (%)	7	10	9	9	6
Amount of rare earth element oxide in glass phase (%)	13.9	12.2	10.7	10.5	16.0
Coefficient of thermal expansion (x 10 ⁻⁶ /oC.)	- 2.0	0.5	- 1.5	- 1.7	- 1.6
Occurrence of cracks	not cracked *	not cracked	not cracked	not cracked	not cracked
Reduction rate in four point bending strength in cooling-heating cycles (%)	1	- 2	2	1	- 1

Remarks

Example

		TABLE 5(c)				
Run No.		56	57	58	59	60
Al2O3 source material		A-3	A-3	A-1	A-5	A-3
TiO2 source material		T-2	T-3	T-3	T-3	T-1
Composition	Al2O3	54.3	69.2	54.3	54.3	54.3
(wt %)	TiO2	42.5	33.8	42.5	42.5	42.5
	SiO2	1.6	3.3	1.6	1.6	1.6
	MgO	1.1	-	-	-	-
	Fe2O3	1.6	-	1.6	1.6	1.6
	Oxide of rare earth element	1.0 (CeO2)	1.25 (Y2O3)	1.0 (CeO2)	1.0 (CeO2)	1.0 (CeO2)
Firing temperature (oC.)		1500	1550	1500	1500	1500
Rapidly Starting cooling temperature condition (oC.)		400	600	400	400	400
Cooling rate (oC./HR)		1000	100	1000	1000	1000
Actual rupture strain		8	4	2	1	2

($\times 10^{-3}$)					
Porosity (%)	12.9	11.1	35.0	12.3	41.3
AT crystal average particle size (μm)	17	12	13	5	8
AT crystal amount (%)	86	79	60	92	59
Glass phase amount (%)	9	10	7	8	7
Amount of rare earth element oxide in glass phase (%)	11.1	12.1	14.1	12.1	13.8
Coefficient of thermal expansion ($\times 10^{-6}$ / $^{\circ}\text{C}$.)	- 1.5	0.9	2.0	- 1.5	2.2
Occurrence of cracks	not cracked	cracked	cracked	cracked	cracked
Reduction rate in four point bending strength in cooling-heating cycles (%)	1	- 2	0	0	0
Remarks	Example		Comparative Example		

From the above, it is clear that according to the ceramic materials for use in insert-casting and the production process therefor, the novel ceramic materials having the actual rupture strain of not less than 6×10^{-3} can be obtained. The ceramic materials according to the present invention have excellent heat resistance, thermal shock resistance, and heat insulation, and are practically excellent products free from occurrence of cracks due to compression forces developed on insert-casting. Thus, the materials are suitable as materials for various liners in exhaust systems including port liners to be brought into high temperature exhaust gases. Therefore, the present invention greatly contributes to industrial development as providing the ceramic materials suitable for insert-casting and the production process therefor, which solve the conventional problems.

CLAIMS: We claim:

[*1] 1. A sintered ceramic material for use in insert casting, comprising:

at least 65% by volume aluminum titanate as a crystalline phase, the diameter of crystals of aluminum titanate being at least 10 μm ; and

a glass intergranular phase present in an amount of not more than 20% by volume, said glass phase comprising a rare earth element in an amount of 0.5-16% by weight when calculated in the form of an oxide;

wherein said sintered ceramic material has a porosity of 5-35%, a four-point bending strength of 0.2-1.7 kgf/mm^2 , a Young's modulus of 50-2,000 kgf/mm^2 and a reduction rate in cooling-heating cycling of not more than 9%.

[*2] 2. The sintered ceramic material according to claim 1, wherein said material has a compression strength of 5 to 40 kgf/mm^2 .

[*3] 3. The sintered ceramic material according to claim 1, further comprising a composition consisting essentially of 40 to 65% by weight of Al_2O_3

and 30 to 65% by weight of TiO₂ as main ingredients.

[*4] 4. The sintered ceramic material according to claim 3, further comprising not more than 10% by weight in total of at least one material selected from the group consisting of SiO₂, MgO and Fe₂O₃.

[*5] 5. The sintered ceramic material according to claim 1, wherein the amount of the rare earth element is not more than 1.8% by weight.

[*6] 6. The sintered ceramic material according to claim 1, wherein said aluminum titanate is present in an amount of at least about 80% by volume.

[*7] 7. The sintered ceramic material according to claim 1, wherein said aluminum titanate is present in an amount of at least about 90% by volume.

[*8] 8. The sintered ceramic material according to claim 1, wherein said sintered ceramic material has a porosity of about 5-14%.

[*9] 9. A sintered ceramic material for use in insert casting, comprising:

at least 65% by volume aluminum titanate as a crystalline phase, the diameter of crystals of aluminum titanate being at least 10 μ m; and

a glass intergranular phase present in an amount of not more than 20% by volume, said glass phase comprising a rare earth element in an amount of 0.5-16% by weight when calculated in the form of an oxide;

wherein said sintered ceramic material has a porosity of 5-35%, a four point bending strength of 0.2-1.7 kgf/mm², an actual rupture strain of not less than 6×10^{-3} and a reduction rate in cooling-heating cycling of not more than 9%.

[*10] 10. The sintered ceramic material according to claim 9, wherein said aluminum titanate is present in an amount of at least about 80% by volume.

[*11] 11. The sintered ceramic material according to claim 9, wherein said aluminum titanate is present in an amount of at least about 90% by volume.

[*12] 12. The sintered ceramic material according to claim 9, wherein said sintered ceramic material has a porosity of about 5-14%.

[*13] 13. The sintered ceramic material according to claim 9, further comprising not more than 17% by volume of a glass containing a rare earth element in an amount of 0.5 to 16% by weight when calculated in the form of an oxide.

[*14] 14. The sintered ceramic material according to claim 9, further comprising a composition consisting essentially of 40 to 65% by weight of Al₂O₃ and 30 to 60% by weight of TiO₂ as main ingredients.

[*15] 15. The sintered ceramic material according to claim 9, further comprising not more than 10% by weight total of at least one material selected from the group consisting of SiO₂, MgO, and Fe₂O₃.

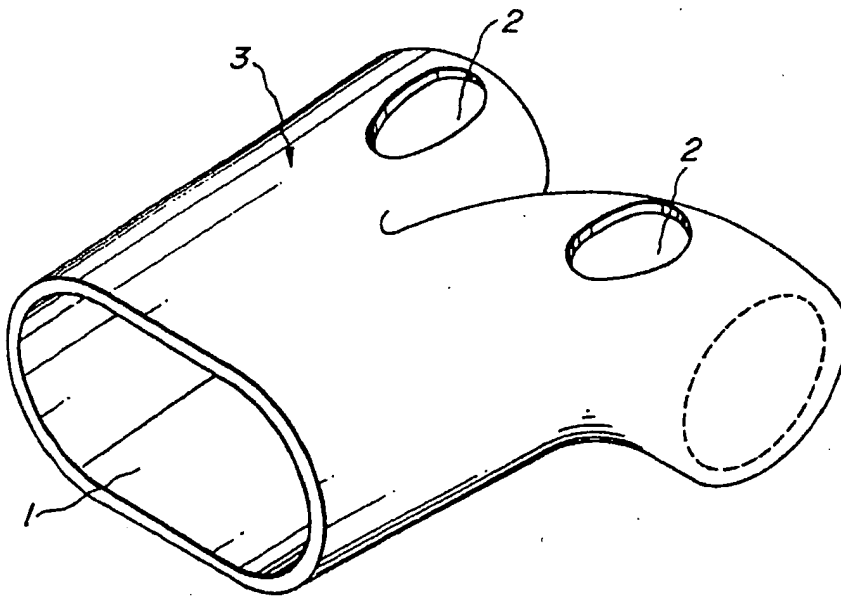
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FIG. 1



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FIG. 2

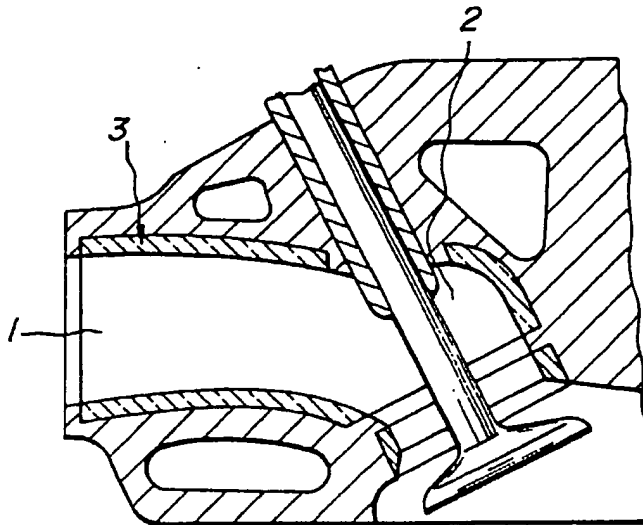
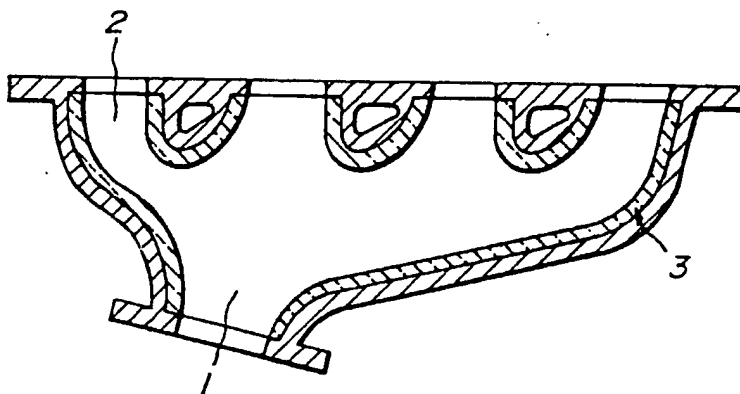


FIG. 3



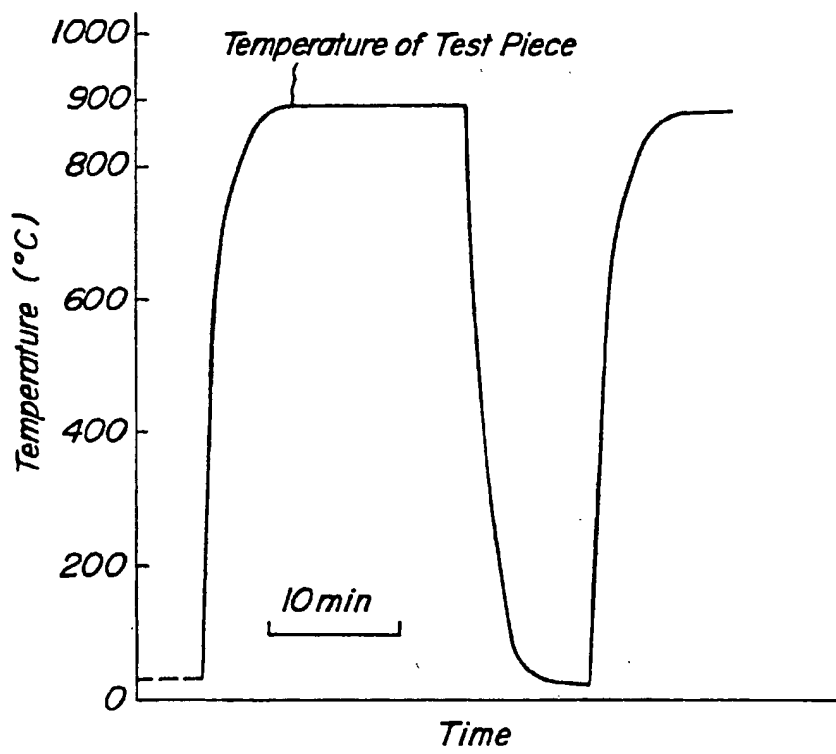
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FIG. 4



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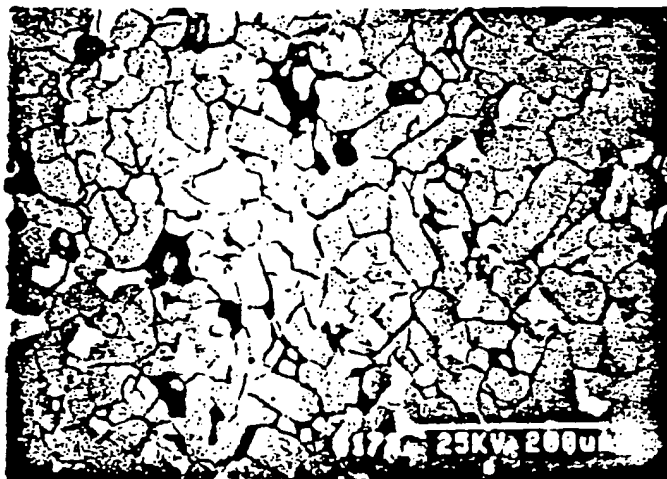
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FIG. 5a



FIG. 5b



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FIG. 6a

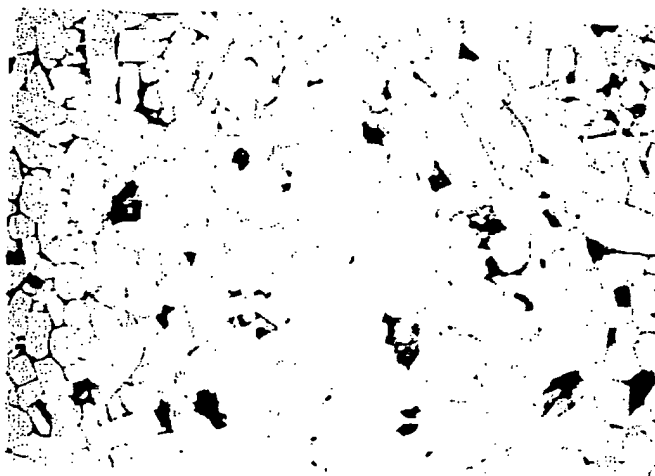
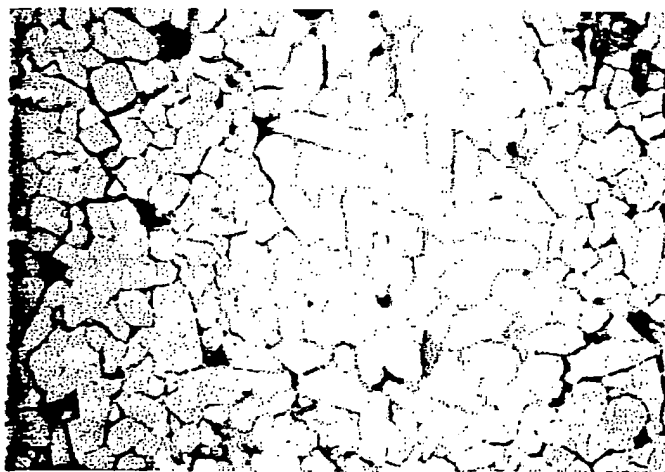


FIG. 6b

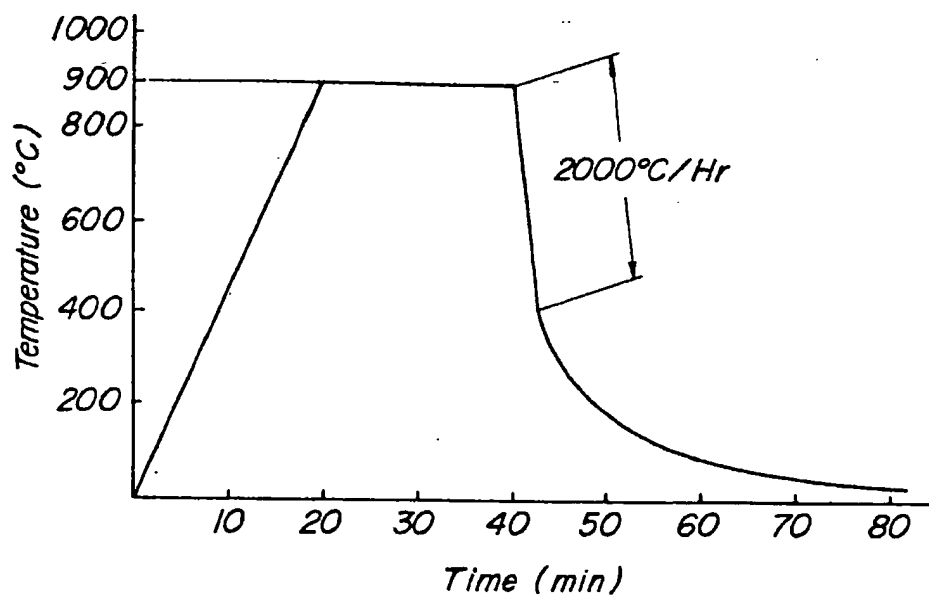


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FIG. 7

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FIG. 8a

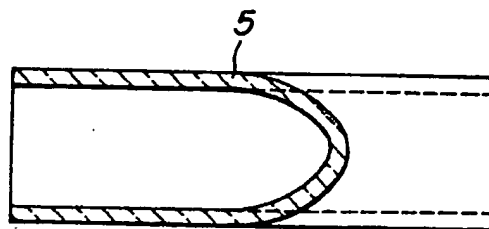
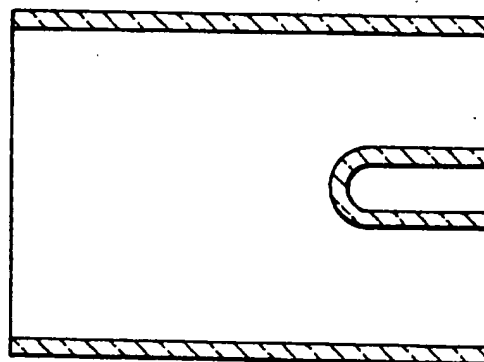


FIG. 8b

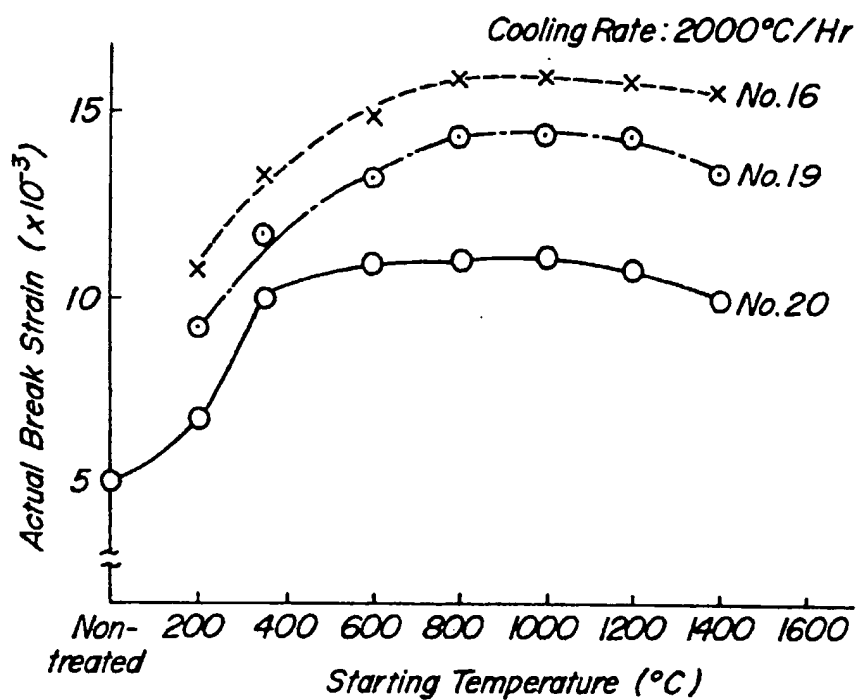


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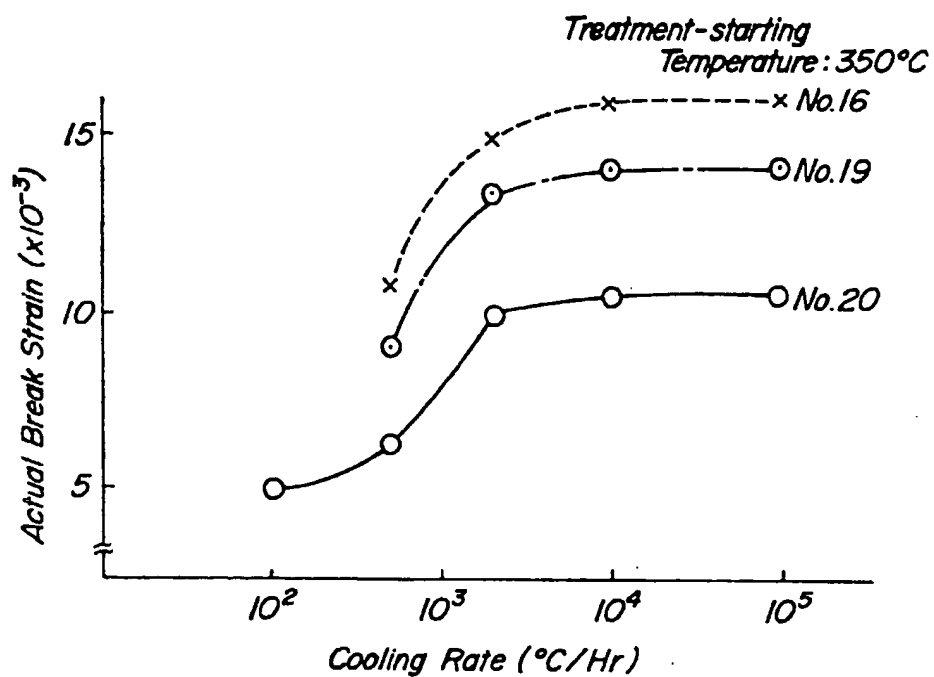
FIG. 9a

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FIG. 9b

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FIG. 10a

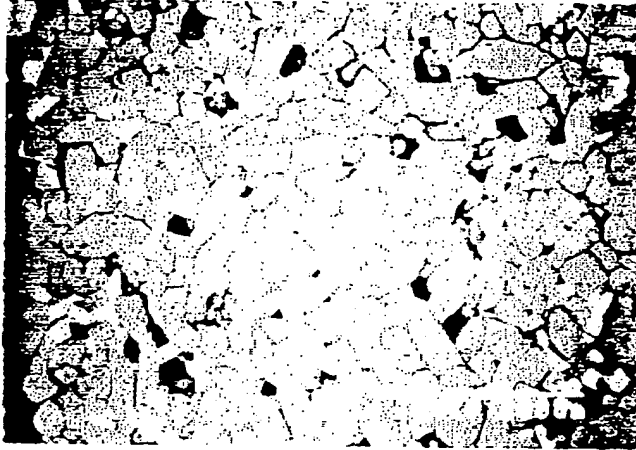


FIG. 10b



8TH PATENT of Level 1 printed in FULL format.

4,895,815

<=2> GET 1st DRAWING SHEET OF 2

Jan. 23, 1990

Sintered form body

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ASSIGNEE-AFTER-ISSUE: Date Transaction Recorded: Aug. 20, 1992

ASSIGNMENT OF ASSIGNORS INTEREST.

CERASIV GMBH INNOVATIVES KERAMIK-ENGINEERING FABRIKSTR. 23 - 29 D-7310

PLOCHINGEN, FED REP GERMANY

Reel & Frame Number: 6223/0535

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FILED: Dec. 3, 1987

CERTCORR: Corrections in Certificate of Correction dated July 9, 1991 are entered herein.

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Feb. 26, 1987 Federal Republic of Germany 3706209

INT-CL: [4] C04B 35#46; C04B 35#10

US-CL: 501#134; 501#153; 501#127; 501#128

CL: 501

SEARCH-FLD: 501#134, 153, 127, 128

REF-CITED:

U.S. PATENT DOCUMENTS

4,277,539	7/1981	* Keller et al.	502#439
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4,526,824	7/1985	* Dworak et al.	502#439

FOREIGN PATENT DOCUMENTS

1471518	10/1969	* Federal Republic of Germany	501#128
3534149	1/1987	* Federal Republic of Germany	501#134
3706209	10/1987	* Federal Republic of Germany	
246977	6/1987	* German Democratic Republic	
57-3767	1/1982	* Japan	501#134

PRIM-EXMR: Dixon, Jr., William R.
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LEGAL-REP: Felfe & Lynch

CORE TERMS: sintered, aluminum, mixture, titanate, thermal, starting, coefficient, impurity, composition, compact, oxide, microns, ratio, density, sintering, green, quartz, grain, magnesium oxide, polished, aluminum oxide, particle, powder, titanium oxide, flexural, composed, compound, molding, mullite, binding

ABST:

Disclosed is a starting mixture for the preparation of a sintered body on a basis of aluminum titanate consists of more than 46 wt.-% TiO₂, up to 49.5 wt.-% Al₂O₃, 3 to 5 wt.-% quartz, and less than 0.2 wt.-% impurities, Al₂O₃ and TiO₂ being present in the weight ratio of 1:0.95 to 1:1.05. The sintered body according to the invention is composed of:

15 to 35 wt.-% TiO₂;

60 to 85 wt.-% Al₂TiO₅ (aluminum titanate);

up to 5 wt.-% Al₂O₃;

up to 17 wt.-% Mullite; and

max. 0.2 wt.-% impurities,

all parts by weight together totaling 100 wt.-%.

Also disclosed are processes for making the sintered body.

NO-OF-CLAIMS: 10

EXMPL-CLAIM: <=6> 1

NO-OF-FIGURES: 4

NO-DRWNG-PP: 2

SUM:

BACKGROUND OF THE INVENTION

The present invention is in a sintered body based on aluminum titanate which is produced from a mixture which contains oxides of aluminum and titanium. The invention furthermore relates to a process for the production of the sintered body and its use.

DE-AS 27 50 290 (U.S. Pat. No. 4,277,539) discloses a silicatic aluminum titanate. The preparation of this known aluminum titanate sets out from 50 to 60

wt.-% of aluminum oxide, 40 to 45 wt.-% of titanium dioxide, 2 to 5 wt.-% of kaolin, and 0.1 to 1 wt.-% of magnesium silicate. The SiO₂ addition is intended to achieve an improved thermal stability of the pure aluminum titanate. However, the reference also states that the addition includes thermal expansion and retards formation of aluminum titanate, so that a higher firing temperature is necessary in order to obtain the same content of aluminum titanate. Also, the MgO component is considered necessary for the improvement of the physical properties. Sepiolite, for example, is proposed for this purpose. This is said to achieve a relatively flat expansion curve, so that the coefficient of thermal expansion is under $1.5 \times 10^{-6} \text{ K}^{-1}$ up to 1000° C. As it appears from the examples of that disclosure, the mixing of aluminum oxide and titanium dioxide is performed in the stoichiometric range (Al₂O₃:TiO₂ = 1:0.78) or with a very slight excess of titanium dioxide. The ratio of Al₂O₃:TiO₂ in Example 5 of that disclosure is 1:0.81. The most favourable results are represented by this example.

The teaching of DE-AS 27 50 290 is thus to be interpreted as recommending the highest possible content of aluminum titanate in the finished body.

DE-AS 12 38 376, discloses production of a ceramic substance from Al₂O₃, SiO₂ and TiO₂. On account of its plasticity, kaolinite is used as the starting component, and also lithium carbonate aluminum hydroxide and other metal oxides. The resulting low strengths of the substance described in DE-AS 12 38 376 are attributed, according to DE-AS 27 50 290, to the lack of a magnesium oxide compound in the starting mixture. These known substances have a coefficient of thermal expansion in the range up to 1000° C. of -0.1 to $-0.8 \times 10^{-6} \text{ K}^{-1}$.

EP-A 133 021 refers to an aluminum titanate-mullite ceramic composed of 60 to 75 wt.-% of Al₂O₃, 15 to 35 wt.-% TiO₂ and 1 to 16.5 wt.-% of SiO₂. Additionally proposed are 0.5 to 5 wt.-% of Fe₂O₃ and/or 0.5 to 5 wt.-% of rare earth metal oxides. The described compositions of the sintered ceramic include mullite contents of 20 to 40 wt.-%, Al₂TiO₅ contents of 50 to 70 wt.-% and Al₂O₃ contents of 10 to 12 wt.-%. Also mentioned are oxides of iron, lanthanum and neodymium in contents of more than 3 wt.-% total. The coefficient of thermal expansion is said to be less than $2.5 \times 10^{-6} \text{ K}^{-1}$ in the range from room temperature to 1000° C.

EP-A 37 868 relates to a ceramic material of low thermal expansion which is made on the basis of aluminum titanate with the addition of magnesium oxide and iron oxide. The main component of the crystalline material phase is given as a solid solution of magnesium oxide/aluminum oxide/titanium oxide/silicon oxide/iron oxide. A number of compounds can be used as starting substances, e.g., kaolin to obtain aluminum oxide, or magnesium carbonate to obtain magnesium oxide. The achievable minimum flexural strength values of about 5 MPa at room temperature, are estimated to be very low. The coefficient of thermal expansion is not to exceed a value of $2 \times 10^{-6} \text{ K}^{-1}$ in the range from 25 to 800° C.

In accordance with U.S. Pat. No. 2,872,726, the addition of chromium oxide, preferably in amounts of 25 to 60 wt.-%, is proposed for a silicate-free material that is made with the use of Al₂O₃ and TiO₂. The achieved flexural strengths are relatively high and are far superior to the strengths which are commonly known for aluminum titanate materials. The ratio of aluminum oxide to

titanium oxide is not mentioned either for the starting mixture or for the composition of the finished material. Only the ratio of oxygen to the individual elemental metal components such as aluminum, titanium and chromium is given.

U.S. Pat. No. 3,534,286 describes a material in which Al_2O_3 is one of the chief components. A typical composition consists of 75.2 wt.-% Al_2O_3 , 22.8 wt.-% Al_2TiO_5 and 2 wt.-% SiO_2 . The presence of free TiO_2 in the solid material is not mentioned. The material is used for scattering microwaves and is to have a low porosity exemplified as a value of up to 7%.

In U.S. Pat. No. 3,607,343 TiO_2 is used in an amount of 1 to 50 vol.-% to coat Al_2O_3 particles. The coated particles are used with the addition of a suitable binding agent, e.g., on the basis of a phenolic resin, for coating by the flame-spraying process.

For the preparation of a sinterable aluminum titanate powder it is proposed according to U.S. Pat. No. 3,825,653 to coprecipitate halogenic or alkoxy compounds of aluminum and titanium and to use the coprecipitate, after drying and calcining, for the sintering of aluminum titanate products. The products manufactured in this manner are said to have a thermal expansion coefficient of less than $1 \times 10^{-6} \text{ K}^{-1}$ in the temperature range of 250 to 1000°C. The density is said to be, depending on the manufacturing process, 70 to 85% of the theoretical density of 3.73 g/cm^3 , i.e., around 2.6 to 3.2 g/cm^3 . Mixtures with a ratio of Al_2O_3 to TiO_2 are given as 1:1, and 1:3 to 3:1. A mixture of silicate compounds is not mentioned. The powder described in the above U.S. patent is used according to U.S. Pat. No. 3,890,140 for the production of melting crucibles for uranium and uranium alloys. The production of the melting crucible by the hot pressing method sets out from an aluminum titanate powder of a size of 10 to 70 microns. A ratio of 50 mol-% each of Al_2O_3 and TiO_2 is considered suitable.

In U.S. Pat. No. 4,118,240 a composition is described which consists essentially of aluminum titanate with the addition of 1.5 to 10 wt.-% of tin dioxide (SnO_2) and 2 to 3 wt.-% of SiO_2 . Instead of SnO_2 , rare earth oxides of, for example, lanthanum, cerium and yttrium are used. A synergetic action between SiO_2 and the rare earth oxides and tin dioxide is expected. The amount of TiO_2 used is about 37 and 38 wt.-% as compared with 53 to 55 wt.-% of Al_2O_3 . In the case of a composition described in this patent, of Al_2O_3 , TiO_2 and SiO_2 , a coefficient of thermal expansion of $1.2 \times 10^{-6} \text{ K}^{-1}$ is achieved in the temperature range of 200 to 1000°C., and a flexural strength at room temperature of (converted) 18 MPa.

In the Federal German publication, H. J. Pohlmann, K. Schricker, D. H. Schuller, Ber. Dt. Keram. Ges., 52 (1975), pages 179 to 183, the properties of the Al_2O_3 - TiO_2 - SiO_2 system are described, kaolin finding application as a source of SiO_2 . As it appears from the structural studies described, these samples contain substantially naught but aluminum titanate as a crystalline phase.

A porous ceramic molding containing more than 80 wt.-% of aluminum titanate, 4 to 10 wt.-% SiO_2 , 0.5 to 5 wt.-% La_2O_3 , CeO_2 and/or Y_2O_3 and Al_2O_3 and TiO_2 is described in U.S. Pat. No. 4,327,188.

DE-AS 25 09 765 describes a wear-resistant, low-friction and corrosion-resistant sintered material based on TiO_2 which contains 1 to 5 wt.-% Al_2O_3 and 1 to 5 wt.-% SiO_2 , balance TiO_2 . The material can also contain a

maximum of 0.1 wt.-% of alkali and alkaline earth oxide.

According to GDR Patent No. 29 794, good thermal shock resistance is produced by a very low, preferably negatively linear thermal expansion coefficient. The compositions proposed according to this patent for the production of a highly refractory, oxidic material with good thermal shock resistance, are those of $\text{MgO-Al}_2\text{O}_3\text{-TiO}_2$ and of $\text{MgO-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$, wherein the TiO_2 content is from 15 to 75 wt.-%, the Al_2O_3 content 70 to 35 wt.-% and the contents of SiO_2 and MgO are up to 40 and 20%, respectively. The linear thermal expansion coefficient achievable with the composition of that patent is said to be less than $4 \times 10^{-6} > K < -1 >$ in the range between 200 and 700°C., or it is to be preferably negative or to differ only slightly from 0. The ratios of admixture of Al_2O_3 to TiO_2 given in the Examples include the broad range of 1:0.7 to 1:1.7, the latter range applying to a silicate-free composition containing 8 wt.-% of MgO .

The last-named disclosure exemplifies the prevailing approach to improving thermal shock resistance of aluminum titanate materials by obtaining the lowest possible thermal expansion coefficient. As it is stated in that patent, the thermal shock resistance is, however, also directly dependent on, among other things, the thermal conductivity, tensile strength and modulus of elasticity. As it appears from the above-mentioned DE-AS 27 50 290, which is believed to be the closest known state of the art, preference is, however, always given to a low thermal expansion coefficient. The disclosed proposals, however, suffer the common disadvantage that the produced sintered articles do not have a thermal shock resistance that is sufficient in every case, so that defects occur either immediately during casting with metal or, under certain circumstances, after the sintered bodies have been in service for an extended period of time. The defects may be initiated by a single contact, e.g., when the article is invested in a molten metal, for example, but do not manifest themselves until later.

It has also been found that the sintered articles in question still have certain differences in quality in spite of careful attention to their physical characteristics, so that premature destruction of the sintered article occurs during its use, even though the stress does not vary. The reasons for this unexpected misbehavior of the sintered articles are not always discernible, but it is assumed that it is the result of certain structural irregularities of the sintered body.

It is thus an object of the present invention to improve the known sintered moldings based on aluminum titanate, and to improve their use in production operations, and especially their stability when invested with molten nonferrous metals in the temperature range below 800°C.

DRWDESC:

Brief Description of the Figures

FIG. 1 shows the natural-untreated-surface of a sintered article according to Example 2 of the invention;

FIG. 2 shows the natural-untreated-surface of a common commercial sintered article;

FIG. 3 shows the polished structure of the sintered article according to FIG. 1; and

FIG. 4 shows the polished structure of the sintered article according to FIG. 2.
DETDESC:

THE PREFERRED EMBODIMENT

Contrary to the previously prevailing notions, the solution to the above-discussed drawbacks is surprisingly achieved with a starting mixture whose composition results in the presence of a relatively high free content of unreacted TiO_2 the finished sintered body. In contrast to the known state of the art, therefore, the added aluminum oxide or titanium oxide is not entirely reacted to aluminum titanate, but care is taken to see that a certain TiO_2 excess is present, which results in the presence of TiO_2 that has not reacted to aluminum titanate.

It has also been found that the quality and uniformity of the sintered bodies of the invention can be further improved by extremely small amounts of magnesium oxide or contents of other impurities, such as those which to some extent unavoidably form.

The present invention is in a mixture for producing a sintered body on a basis of aluminum titanate, the mixture comprising:

more than 46 wt.-% TiO_2 ;

up to 49.5 wt.-% Al_2O_3 ;

3 to 5 wt.-% quartz (SiO_2);

less than 0.2 wt.-% impurities, Al_2O_3 and TiO_2 being present in a weight ratio of 1:0.95 to 1:1.05, and all weight parts together make up 100 weight-percent.

Even though it is not yet understood in detail to what the superior effect of the sintered body according to the invention is to be attributed, it has nevertheless been found that the following features are especially important:

(1) the composition of the starting mixture of high-purity substances, which includes the avoidance of kaolin which is known as a component of the starting mixture in the state of the art;

(2) an aluminum oxide with a purity of at least 99% is advantageously used; and

(3) the presence of a maximum of 0.2 wt.-% of impurities, such as magnesium oxide, which however is in no case necessary, and can be present in a maximum of up to 0.1 wt.-%, because the presence of this substance in the starting mixture cannot always be excluded, since it is unavoidable as an impurity, e.g., as detritus from grinding.

It is important that the titanium oxide phase is uniformly distributed in the sintered compact. A uniform distribution of titanium oxide is achieved by intimately grinding and mixing the starting mixture. Preferred milling machines

are attrition mills, vibration mills and rotation mills. The milling time ranges from 5 to 15 h. It has been found that the presence of a uniformly dispersed TiO_2 phase, when the starting mixture according to the invention is used, results in a most extensively crack-free polished structure in the sintered compact. The presence of a largely crack-free polished structure is very important because the improved safety of the sintered compacts according to the invention in production operations is to be attributed thereto.

It is also important that the aluminum titanate grains have an average size of 5 to 20 microns; preferably even 8 to 15 microns. The average grain size of the titanium oxide is lower, and is around 0.5 to 10 microns, but in any case it is smaller than the average grain size of the aluminum titanate grains. The known sintered compacts of aluminum titanate from mixtures of the oxides of aluminum and titanium with SiO_2 have, in contrast, an aluminum titanate grain size of 1 to 3 microns.

The invention is also in a sintered body which is composed of:

15 to 35 wt.-% TiO_2 ;

60 to 85 wt.-% Al_2TiO_5 (aluminum titanate);

up to 5 wt.-% Al_2O_3 ;

up to 17 wt.-% Mullite; and

max. 0.2 wt.-% impurities;

all parts by weight together totaling 100 wt.-%.

The density of the sintered body is at least 3.0 g/cm^3 , but in contrast to the known compacts it can increase to as much as 3.6 g/cm^3 . The density is preferably in the range of from 3.3 to 3.5 g/cm^3 . The flexural strength is at least 25 MPa and preferably in the area of 33 to 47 MPa. The elastic modulus is about 14000 to 25000 MPa. The coefficient of expansion is 1.5 to $3.0 \times 10^{-6} \text{ K}^{-1}$ in the temperature range from 400°C to 800°C and thus is substantially higher than that of the known sintering compacts according to DE-AS 27 50 290. The thermal conductivity amounts to 1-3 W/mK.

In other advantageous embodiments of the invention, importance is attached to the method of producing the compact according to the invention. The starting mixture must be composed of high-purity substances, from which the previously proposed kaolin must be expressly excluded. The necessary SiO_2 doping is performed in the form of quartz, while the presence of additional impurities is to be excluded insofar as possible. The maximum content of impurities must not, however, exceed 0.2% of the weight of the starting mixture and a maximum of 0.1 wt.-% of magnesium oxide is permissible. A green body or compact of a density of at least 2.4 g/cm^3 is made from a slip prepared, using known adjuvants, by mix-grinding the oxides to a D50 grain size under 0.5 microns. The sintering is performed at temperatures of 1350°C to 1490°C for a period of 1 to 5 hours.

Alternatively, the compacts can also be produced by molding and pressing a powder mixture of the composition according to the invention, which contains a commonly used binding agent and is obtained by spray drying. The sintering is

then performed in the above-stated temperature range for the stated period of time.

After the sintering process, the sintered body is brought to its final shape by methods known in themselves, e.g., by machining with diamond tools. An especially important field of application of the sintered articles according to the invention is their use in the production of compound bodies consisting of the sintered body recasted with metal. In this case the sintered body is hollow in the manner of a tube. Such compound bodies are, for example, exhaust pipes in internal combustion engines, especially in the area of the combustion chamber. It is especially advantageous in this case if the sintered compact is in every cross section round or oval, a concave shape is avoided, and all edges are rounded. Preferably the wall thickness is between 2 and 6 mm. Especially preferred is a wall thickness of 3 to 4 mm.

The following Examples will serve for the further explanation of the invention.

EXAMPLE 1

A starting mixture of:

49 wt.-% Al_2O_3 ,

47 wt.-% TiO_2 , and

4 wt.-% quartz (SiO_2)

is dispersed in water and the slip is ground in a vibration mill for 10 h to a D50 particle size of less than 0.5 microns. After the addition of 2% of polyvinyl alcohol as temporary binding agent, the mixture is spray dried and made into a compact by pressing at a pressure of 1000 bar. The binding agent is burned out at 300°C. and the molding is then sintered for 3 h at 1430°C. The following values are measured on the sintered compact:

Density: 3.43 g/cm³

Flexural strength ρ_B : 38 MPa

Modulus of elasticity: 18000 MPa.

Thermal expansion coefficient in the temperature range from 400°C to 800°C:
 $2.3 \times 10^{-6} \text{ K}^{-1}$

The sintered molding is composed of:

68 wt.-% Al_2TiO_5 ,

18 wt.-% TiO_2 , homogeneously dispersed

1 wt.-% Al_2O_3 , and

balance mullite.

EXAMPLE 2

A watery slip without binding agent is prepared with a solid content of 75 wt.-% and a particle size after grinding for six hours in a vibration mill to $D_{50} < 0.5$ microns and the following composition:

48.5 wt.-% Al_2O_3 ,
48.5 wt.-% TiO_2 ,
3 wt.-% quartz (SiO_2).

A hollow, tube-like body is formed from the slip by casting and this green body is sintered at 1440° C. for a period of 2.5 hours.

The following values were measured on the sintered product:

Density: 3.4 g/cm³ >

Flexural strength ρ_B : 36 MPa

Elastic modulus: 15000 MPa

Thermal expansion coefficient in the temperature range from 400° to 800° C:
 $2.1 \times 10^{-6} < K^{-1} >$

The sintered product is composed of:

72 wt.-% Al_2TiO_5 ,
18 wt.-% TiO_2 , homogeneously dispersed
1 wt.-% Al_2O_3 , and
balance mullite.

A comparison of FIGS. 1 and 2 shows the substantially coarser grain of the sintered molding according to the invention.

Comparison of FIGS. 3 and 4 shows, in the case of the sintered article according to the invention, a crack-free polished structure with a uniform distribution of TiO_2 , whereas FIG. 4 shows a network of cracks in the polished structure.

It will be understood that the specifications and examples are illustrative but not limitative of the present invention and that other embodiments within the spirit and scope of the invention will suggest themselves to those skilled in the art.

CLAIMS: We claim:

[*1] 1. A mixture for producing a sintered body on a basis of aluminum titanate, the mixture consisting essentially of:

more than 46 wt.-% TiO_2 ;
up to 49.5 wt.-% Al_2O_3 ;

3 to 5 wt.-% quartz (SiO₂);

less than 0.2 wt.-% impurities, the Al₂O₃ and TiO₂ being present in a weight ratio of 1:0.95 to 1:1.05, and all weight parts together make up 100 weight-percent.

[*2] 2. A sintered body consisting essentially of:

15 to 35 wt.-% TiO₂;

60 to 85 wt.-% Al₂TiO₅ (aluminum titanate);

up to 5 wt.-% Al₂O₃;

max. 0.2 wt.-% impurities; and

up to 17 wt.-% mullite,

all weight parts together making up 100 weight-percent.

[*3] 3. The sintered body of claim 2 having a density of 3.0 to 3.6 g/cm³

[*4] 4. The sintered body of claim 2 having a polished structure with a homogeneous distribution of the TiO₂ phase.

[*5] 5. The sintered body of claim 2 having an average thermal expansion coefficient of $1.5 \text{ to } 3.0 \times 10^{-6} \text{ K}^{-1}$ in the range from 400° to 800° C.

[*6] 6. The sintered body of claim 2 wherein the aluminum titanate has an average grain size of about 5 to 20 microns.

[*7] 7. A method of preparing the sintered body of claim 2 comprising: wet grinding to a D50 particle size < 0.5 microns a starting mixture of

more than 46 wt.-% TiO₂,

up to 49.5 wt.-% Al₂O₃,

3 to 5 wt.-% quartz (SiO₂),

less than 0.2 wt.-% impurities,

the Al₂O₃ and TiO₂ being present in a weight ratio of 1:0.95 to 1:1.05,

all weight-parts making up 100 wt.-% to form a wet ground mixture; forming a slip from the wet ground mixture; forming a green body from the slip; drying the green body to form a dried body having a green density of at least 2.4 g/cm³; and sintering the dried green body at a temperature of 1350° to 1490° C. to form the sintered body.

[*8] 8. The method of claim 7 wherein the sintering is for a period of 1 to 5 hours.

[*9] 9. A method of preparing the sintered body according to claim 2 comprising: wet grinding to a D50 particle size < 0.5 microns a starting mixture of

more than 46 wt.-% TiO₂,

up to 49.5 wt.-% Al₂O₃,

3 to 5 wt.-% of quartz (SiO₂),

less than 0.2 wt.-% impurities,

the Al₂O₃ and TiO₂ being present in a weight ratio of 1:0.95 to 1:1.05,

all parts by weight making up 100 wt.-% to form a wet ground mixture; forming a slip from the wet ground mixture; adding a binding agent to the slip; spray drying the mixture to form a powder mixture; pressing the powder mixture to form a green body which has a green density of at least 2.4 g/cm³; and sintering the green body at a temperature of 1350° to 1490° C. to form the sintered body.

[*10] 10. The method of claim 9 wherein the sintering is for a period of 1 to 5 hours.

U.S. Patent

Jan. 23, 1990

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4,895,815

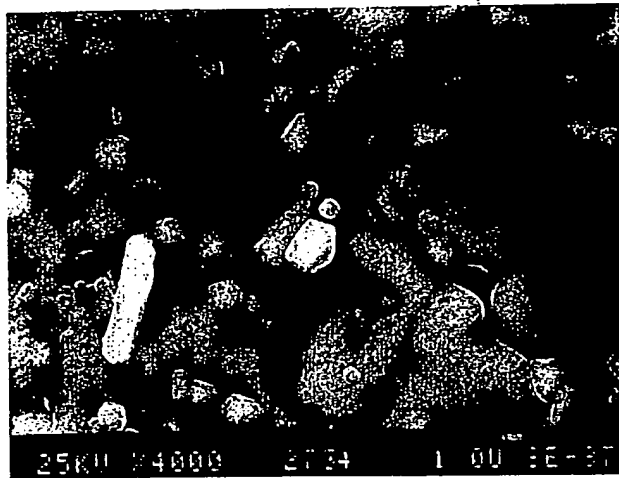


FIG. 1

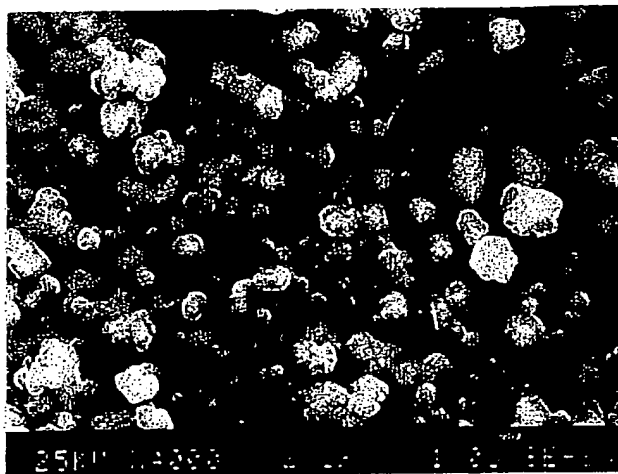


FIG. 2

U.S. Patent

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4,895,815

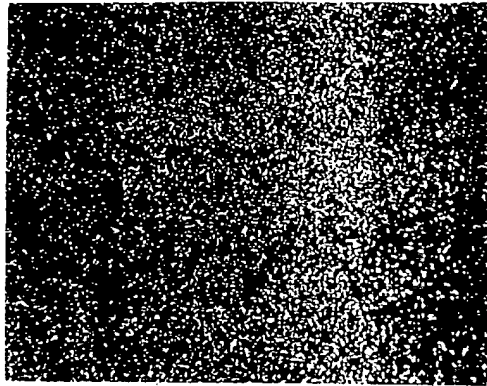


FIG. 3

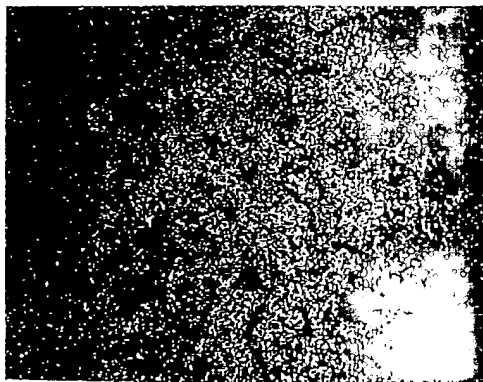


FIG. 4

4TH PATENT of Level 1 printed in FULL format.

5,153,153

Oct. 6, 1992

Sintered ceramic materials based on aluminium titanate, a
process for their production and their use

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CL: 501

SEARCH-FLD: 501#134, 136, 128, 131, 127

REF-CITED:

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PRIM-EXMR: Group, Karl

LEGAL-REP: Connolly and Hutz

CORE TERMS: decomposition, ceramic, sintered, resistance, titanate, aluminium, sintering, oxidizing, composition, kaolin, powder, lattice, mullite, cat, magnesium, thermal, tialite, iron, d50, modulus, batch, phase, mixture, raw, iron-containing, shrinkage, chemical, fracture, strain, oxide

ABST:

Sintered ceramic material which comprises doped aluminum titanate and mullite having the composition:

50-61.5% by weight Al_2O_3 ,

36-47.5% by weight titanium oxide, expressed as TiO_2 ,

2.5-5% by weight SiO_2 ,

with the sum total of the three components adding up to 100%, and which further comprises 0.3 to 1% by weight MgO and up to 1% by weight impurities, useful as, inter alia, filters, catalyst supports and internal combustion engine parts, are prepared by mixing and shaping materials of suitable composition and then sintering the shaped composition at temperatures of 1250° to 1600° C. over a holding time of 0.5 to 100 hours.

NO-OF-CLAIMS: 15

EXMPL-CLAIM: <=11> 1

NO-OF-FIGURES: 0

NO-DRWNG-PP: 0

SUM:

This invention relates to sintered ceramic material based on the main phases of doped aluminium titanate and mullite having the following composition:

50 to 61.5% by weight Al_2O_3 ,

36 to 47.5% by weight titanium oxide, expressed as TiO_2 ,

2.5 to 5% by weight SiO_2 ,

the sum total of the three components being 100%, and up to 1% by weight impurities, to processes for the production of these sintered moldings and to their use.

BACKGROUND OF THE INVENTION

Materials which retain their thermomechanical properties, particularly strength and thermal shock resistance, even under extremely reducing conditions, are required in process engineering and particularly in melt metallurgy.

Although ceramics based on pure aluminium titanate or tialite show interesting properties, such as a low thermal expansion coefficient (TEC) and a low Young's modulus, they are of only limited technological value on account of their very poor strength and their tendency to decompose at temperatures in the range from about 900° to 1300° C. At temperatures in this range, tialite decomposes into the starting oxides Al_2O_3 and TiO_2 , accompanied by a pronounced increase in the TEC and a correspondingly inadequate thermal shock resistance.

Numerous attempts have been made to counteract this tendency towards decomposition. Thus, U.S. Pat. No. 2,776,896 refers to the stabilizing effect of iron solid solutions in Al_2TiO_5 . SiO_2 and MgO also show a stabilizing effect, although it is not as pronounced as in cases where the preferred Fe_2O_3 is added. However, it is pointed out that additions of SiO_2 and MgO can be used for stabilization when the electrical properties, the color or the susceptibility to reduction of the iron-containing aluminium titanate are not wanted.

The superiority of iron stabilization is also described in DE-A 3 814 079, according to which an adequate Fe_2O_3 concentration is responsible for long-term stabilization.

This no longer applies when the stability of aluminium titanate under strongly reducing or varying atmospheres is investigated. Thus, an Al_2TiO_5 ceramic stabilized solely with additions of Fe_2O_3 shows signs of decomposition in a pure CO atmosphere at a temperature of 1050° C.

The problem addressed by the present invention was to provide an inexpensive aluminium titanate ceramic which would show sufficient resistance to decomposition at temperatures of $\geq 1000^\circ\text{C}$. both under strongly reducing conditions (for example CO) and under oxidizing conditions (for example air) to retain its thermomechanical properties, particularly its strength and thermal shock resistance.

There are only limited references in the prior art to improving the susceptibility of aluminium titanate ceramic to reduction. Thus, U.S. Pat. No. 4,118,240 describes additions of 1.5 to 10% by weight SnO_2 and 2 to 13% by weight SiO_2 or 0.5 to 10% by weight rare earth oxide and 2 to 13% by weight SiO_2 . Samples are said to show improved resistance to decomposition, even under reducing conditions. Flexural strength at room temperature is only of the order of 18 to 35 MPa.

Although there is much more patent literature relating to SiO_2 -, MgO - and Fe_2O_3 - containing aluminium titanate ceramic, there are no apparent solutions to the problem stated above.

EP-B 37 868 describes an aluminium titanate ceramic containing 1 to 20% by weight SiO_2 (preferably 2 to 15% by weight), 1.2 to 20% by weight MgO (preferably 2 to 17% by weight) and 0.5 to 20% by weight Fe_2O_3 (preferably 2 to 10% by weight). Flexural strengths of only 7 to 35 MPa are measured at room temperature.

EP-A 210 813 describes a low-glass aluminium titanate/mullite ceramic containing at least one presynthesized component, namely aluminium titanate and/or mullite. The ceramic contains at least 1.2% by weight Fe_2O_3 . For a maximum MgO content of 0.8% by weight, the $\text{MgO}:\text{Fe}_2\text{O}_3$ ratio is ≥ 0.67 .

Resistance to decomposition under highly reducing conditions is not guaranteed.

DD-B 29 794 claims an aluminium titanate ceramic containing additions of 0 to 40% by weight SiO_2 and 0 to 20% by weight MgO . In addition, 0.05 to 15% by weight of the oxides Zn, Ca, Ba, Fe, Ni, Cu, Mn and Cr may be added. In Example 4, 20% by weight MgO and 1.5% by weight Fe_2O_3 are added, which gives a ceramic of insignificant strength.

DE-C 2 750 290 describes a silicate-containing aluminium titanate ceramic produced from a raw material mixture containing 2 to 5% by weight kaolin and 0.1 to 1% by weight magnesium silicate. Under the assumption that the magnesium silicate is sepiolite (column 4, line 36), this corresponds to an SiO_2 content of 1.0 to 2.9% by weight and to an MgO content of 0.025 to 0.25% by weight. The material calcined at temperatures of 1350° to 1450° C. has strengths of 30 to 40 MPa (Examples 4 and 5), a Young's modulus of approximately 13 GPa and a TEC (measured in the range from 25° to 1000° C.) of $1.3 \text{ to } 1.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$. There are no quantitative references to the resistance to decomposition under reducing or oxidizing conditions.

DE-A 3 644 664 describes an aluminium titanate ceramic containing four additives, namely: 2.5 to 3.0% by weight SiO_2 , 0.5 to 1.0% by weight MgO , 0.1 to 1.5% by weight Fe_2O_3 (preferably 0.5 to 1% by weight) and 0.1 to 2.5% by weight La_2O_3 (preferably 0.5 to 2.0% by weight). The Example contains 2.56% by weight SiO_2 , 0.74% by weight MgO , 0.74% by weight Fe_2O_3 and 1.96% by weight La_2O_3 . After heating for 100 h at 1100° C. (there is no mention of the atmosphere), this ceramic still contains 61% Al_2TiO_5 . However, this ceramic is not sufficiently resistant to decomposition under reducing conditions.

BRIEF DESCRIPTION OF THE INVENTION

A sintered ceramic body based on aluminium titanate has now surprisingly been found which eminently satisfies the above-stated requirement of improved resistance to decomposition both under strongly reducing conditions and under oxidizing conditions. To this end, it need only contain the two inexpensive additives from the system of silicon and magnesium. Thus, the ceramic bodies of the present invention contain mostly aluminium oxide and titanium oxide but also contain 2.5 to 5% by weight silicon dioxide and 0.3 to 1% by weight of magnesium oxide. These phase composition is mainly aluminium titanate solid solution and mullite solid solution.

DETDESC:

DETAILED DESCRIPTION

The material according to the invention, which is described in detail hereinafter and which is produced by careful selection of the composition and correspondingly adapted process management, particularly during sintering, satisfies all the technical and economic requirements stated above.

The present invention relates to sintered ceramic bodies based on the main phases of doped aluminium titanate and mullite which has the following chemical composition:

50 to 61.5% by weight Al_2O_3 ,

36 to 47.5% by weight titanium oxide, expressed as TiO_2 ,

2.5 to 5% by weight SiO_2 ,

the sum total of the three components adding up to 100%, and up to 1% by weight impurities, characterized in that the sintered molding additionally contains 0.3 to 1% by weight MgO .

In its calcined state, the material according to the invention essentially consists of two crystalline phases, namely: an Mg-doped Al_2TiO_5 phase and the mullite phase which is assumed to be $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

The optimal MgO content is a compromise between the requirements of maximum resistance to decomposition, maximum fracture strain and minimum shrinkage during sintering.

It has surprisingly been found that the resistance to decomposition under reducing conditions falls distinctly at Mg concentrations (expressed as MgO) below 0.3% by weight whereas resistance to decomposition under oxidizing conditions remains substantially constant in the range investigated. At MgO contents above 1% by weight, there is a further reduction in fracture strain. However, a high fracture strain is crucial to the thermal shock resistance required. In addition, there is a further increase in shrinkage during sintering; the higher the shrinkage during sintering, the more difficult it is to keep to the narrow tolerances with "as-fired" components.

In one preferred embodiment, therefore, the sintered molding according to the invention has an MgO content of 0.3 to 0.6% by weight.

Numerous decomposition tests have shown that, although increased iron concentrations improve resistance to decomposition under oxidizing conditions, they also impair the resistance to decomposition under reducing conditions. In one preferred embodiment, the sintered ceramic according to the invention additionally has an iron oxide content of 0.015 to 0.5% by weight and, more preferably, in the range from 0.05 to 0.4% by weight, expressed as Fe_2O_3 . The % by weight ratio of MgO to Fe_2O_3 is preferably between 20 and 2.

The SiO_2 content is also a compromise between various requirements, including maximum resistance to decomposition, minimum Young's modulus and minimum coefficient of thermal expansion. Both the TEC and the Young's modulus increase with increasing SiO_2 content, so that the thermal shock resistance is adversely affected. Accordingly, the upper limit is at 5% by weight SiO_2 . In view of the poor resistance to decomposition under oxidizing conditions, the lower limit is at 2.5% by weight and preferably at 3% by weight.

Sintered bodies according to the invention show particularly high resistance to decomposition when the sum total of the contents of unreacted Al_2O_3 and TiO_2 is $\leq 5\%$ by weight, preferably $\leq 2.5\%$ by weight.

The sintered moldings according to the invention are distinguished by a combination of particularly favorable physical properties. Thus, their flexural strength at room temperature is in the range from 40 to 80 MPa, their Young's modulus is between 5 and 25 GPa and their TEC (RT-1000°C) is in the range from $0-2.5 \times 10^{-6} > 1/\text{K}$. Resistance to decomposition is guaranteed, even after

more than 100 hours at 1000° C. both under oxidizing and under reducing conditions. The accelerated decomposition tests under oxidizing and reducing conditions reveal a tialite content of more than 60% by weight in the decomposition test under oxidizing conditions and more than 75% by weight in the decomposition test under reducing conditions.

Another advantage and characteristics feature of the sintered ceramic according to the invention is that they can be sintered at relatively low temperatures with short holding times. The ceramic is sintered at temperatures of 1250° to 1600° C. and preferably at temperatures of 1300° to 1450° C. with a holding time of 0.5 to 100 hours and preferably with a holding time of 1 to 50 hours.

Accordingly, the present invention also relates to a process for the production of the sintered ceramic body according to the invention, characterized in that it comprises the steps of mixing, shaping and sintering suitable materials.

Shaping may be carried out in known manner by slip casting. Shaping may also be carried out by molding and pressing a powder mixture having the composition according to the invention which contains the usual binders. It has proved to be of particular advantage to use the raw materials predispersed by wet grinding with subsequent granulation drying; the raw materials may either be individually wet-ground and subsequently mixed before granulation drying or may be wet-ground together in the form of a mixture. These granules provide for much shorter dispersion times in the preparation of the slip than where the individual components are used. In addition, the presence of only one premixed component provides for simpler storage and for better dosability than in cases where several components differing their apparent densities are used.

In addition, the dried granules are particularly suitable for dry pressing.

In one particularly preferred variant of the process according to the invention, therefore, the components are predispersed individually or in admixture by wet grinding, preferably by grinding in an attritor mixture of wet-ground components is subsequently processed by granulation drying, preferably by spray drying, and used as the raw material.

Sintering is preferably carried out by reaction sintering under the conditions mentioned above. Pre-reacted mixtures may also be successfully used. After sintering, the sintered ceramic body may be finished by known methods.

In one particularly advantageous embodiment, the magnesium compounds are introduced in the form of magnesium titanates, such as Mg_2TiO_4 , $MgTiO_3$ and/or $MgTi_2O_5$. In practice, the use of magnesium titanate provides for a slip having a relatively high solids content for reduced shear thinning behavior. Another advantage of using magnesium titanate powder lies in its high reactivity. Another advantage of the synthetic magnesium over natural raw materials is its purity. The natural raw materials contain in particular alkali and calcium impurities which lead to a reduced resistance to decomposition in aluminium titanate ceramic.

In one preferred embodiment of the process according to the invention, the iron compounds were introduced into the mixture in the form of finely disperse alpha - Fe_2O_3 powder and/or preferably in the form of iron-containing layer

silicates and, more preferably, in the form of iron-containing clays or kaolin.

Comparison of various iron raw material sources shows that iron-containing clays or kaolins are of particular advantage. One particular advantage of natural aluminium silicates lies in the fact that the clays/kaolins additionally represent an extremely inexpensive SiO_2 and Al_2O_3 raw material source.

The present invention also relates to the use of the sintered ceramic bodies according to the invention. They are particularly suitable for the production of hollow tube-like metal/ceramic composites. They are also suitable for reinforcing engine pistons and cylinder heads and as an incorporated element in catalysts, e.g. as spacer rings.

Another use is as a catalyst support, optionally after doping with catalytically active substances.

Another use is as filters, particularly as particle filters in diesel engines, optionally after doping with catalytically active substances and addition of porosity promoters.

By virtue of their favorable thermal and mechanical properties, the sintered materials according to the invention are also suitable for use as a material in melt metallurgy.

The following Examples are intended to illustrate the invention without limiting it in any way.

EXAMPLES

Batches having various MgO concentrations were compared. The raw materials used were Al_2O_3 powder (corundum, $d_{50} < 0.5 \mu\text{m}$), TiO_2 powder (rutile, $d_{50} < 0.5 \mu\text{m}$), MgTiO_3 powder ($d_{50} < 0.8 \mu\text{m}$) and an iron-containing kaolin, the batch being calculated in accordance with the composition shown in Table I. After the addition of 30% by weight water and commercially available dispersants, the powders were ground for 12 hours to form a slip. The slip-cast hollow bodies were dried and then sintered for 5 hours at 1440°C . Quantitative phase analysis by X-ray diffractometry was carried out on the sintered body both as fired and as well after an additional decomposition test under oxidizing conditions (40 hours, 1100°C ., static air) and after a decomposition test under reducing conditions (20 hours, 1050°C ., CO atmosphere, flowing). Assuming equilibrium conditions, the reducing atmosphere corresponds to an oxygen partial pressure p_{O_2} approximately equal 10^{-18} atm. Fracture strain was calculated from the flexural strength at room temperature and the static Young's modulus elasticity. The linear sintering shrinkage was calculated from the green and sinter densities.

The results in Table I show that the resistance to decomposition under reducing conditions falls drastically below 0.3% by weight MgO in contrast to the resistance to decomposition under oxidizing conditions. Above 1% by weight MgO , the decreasing fracture strain and increasing sintering shrinkage reach very unfavorable values.

TABLE I

Resistance to decomposition, fracture strain and shrinkage on sintering for samples of different Mg content

	1 (Comparison)	2 (Comparison)	* 3	* 4	5 (Comparison)
Example					
Cat. % Mg in the tialite lattice	0.2	0.4	0.6	1.0	2.0
Cat. % Fe in the tialite lattice	0.14	0.14	0.14	0.14	0.14
Raw materials	Al ₂ O ₃ , TiO ₂ Kaolin (Fe) MgTiO ₃	Al ₂ O ₃ , TiO ₂ Kaolin (Fe) MgTiO ₃	Al ₂ O ₃ , TiO ₂ Kaolin (Fe) MgTiO ₃	Al ₂ O ₃ , TiO ₂ Kaolin (Fe) MgTiO ₃	Al ₂ O ₃ , TiO ₂ Kaolin (Fe) MgTiO ₃
Chemical composition [% by weight]					
Al ₂ O ₃	57.67	57.35	57.02	56.38	54.76
TiO ₂	38.72	38.93	39.14	39.56	40.61
SiO ₂	3.48	3.48	3.48	3.47	3.46
MgO	0.13	0.24	0.36	0.59	1.17
Fe ₂ O ₃	0.16	0.16	0.16	0.16	0.16
Sintering conditions	5 h/1440° C.	5 h/1440° C.	5 h/1440° C.	5 h/1440° C.	5 h/1440° C.
Al ₂ TiO ₅ content [% by weight]					
as fired	91	95	92	90	90
Decomposition test - oxidizing	80	78	76	78	82
Decomposition test - reducing	7	77	85	91	86
Fracture strain [0/00]	2.9	2.6	2.4	2.4	2.1
Linear shrinkage after sintering [%]	10.6	11.5	12.3	13.1	14.2

The influence of the MgO:Fe₂O₃ ratio is demonstrated by the results in Table II.

The three batches mentioned were prepared from TiO₂ powder (rutile, d₅₀ < 0.5 μm), Al₂O₃ powder (corundum, d₅₀ < 0.5 μm), SiO₂ powder (d₅₀ < 0.3 μm), MgTiO₃ powder (d₅₀ < 0.8 μm) and Fe₂O₃ powder (d₅₀ < 0.2 μm); the compositions correspond to Table II.

All three batches were calculated so that 0.8 cat.-%, i.e. 0.8% of all the cations in the Al₂TiO₅ lattice, are substituted by Mg or Mg + Fe. The calculation was based on the simplifying assumption that Mg and Fe are incorporated exclusively in the tialite lattice. The results shown confirm the fact known from the literature that even small Fe-additions produce a distinct improvement in the resistance to decomposition under oxidizing conditions. What is unexpected, however, is that these additions greatly impair the resistance to decomposition under reducing conditions.

TABLE II
Resistance to decomposition under oxidizing and reducing
conditions for samples having different Mg:Fe ratios,
Mg + Fe [cat.-%] = const.

Example	6	7	8
Cat. % Mg in the Al ₂ TiO ₅ lattice	0.8	0.6	0.4
Cat. % Fe in the Al ₂ TiO ₅ lattice	-	0.2	0.4
Raw materials	Al ₂ O ₃ , TiO ₂ SiO ₂ , MgTiO ₃ Fe ₂ O ₃	Al ₂ O ₃ , TiO ₂ SiO ₂ , MgTiO ₃ Fe ₂ O ₃	Al ₂ O ₃ , TiO ₂ SiO ₂ , MgTiO ₃ Fe ₂ O ₃
Chemical composition [% by weight]			
Al ₂ O ₃	55.96	56.10	56.23
TiO ₂	40.94	40.68	40.42
SiO ₂	2.61	2.61	2.61
MgO	0.49	0.38	0.25
Fe ₂ O ₃	-	0.24	0.48
Sintering conditions	5 h/1400° C.	5 h/1400° C.	5 h/1400° C.
Al ₂ TiO ₅ content [% by weight]			
Sintered	96	97	94
Decomposition test, oxidizing	32	62	68
Decomposition test, reducing	75	25	4

Influence of the Fe Raw Material Source

Two batches having the same global chemical composition are compared in the Table III. The difference is that silicon and iron are introduced on the one hand through two raw materials- > 98% pure SiO₂ powder (d₅₀ < 0.3 μm) and Fe₂O₃ powder (d₅₀ < 0.3 μm)-and on the other hand through a single raw material-kaolin containing 1.5 to 2% by weight Fe₂O₃. The results in Table III show that the iron introduced through the kaolin contributes to a much better resistance to decomposition under oxidizing and reducing conditions.

TABLE III
Resistance to decomposition under oxidizing and reducing
conditions for samples with different SiO₂ and Fe₂O₃ raw
material sources

Example	9	3
Cat. % Mg in the Al ₂ TiO ₅ lattice	0.6	0.6
Cat. % Fe in the Al ₂ TiO ₅ lattice	0.14	0.14
Raw materials	Al ₂ O ₃ , TiO ₂ SiO ₂ , MgTiO ₃ Fe ₂ O ₃	Al ₂ O ₃ , TiO ₂ Kaolin (Fe) MgTiO ₃

Chemical composition

[% by weight]

Al ₂ O ₃	56.89	57.02
TiO ₂	39.12	39.14
SiO ₂	3.47	3.48
MgO	0.36	0.36
Fe ₂ O ₃	0.16	0.16
Sintering conditions	5 h/1440o C.	5 h/1440o C.
Al ₂ TiO ₅ content		
[% by weight]		
Sintered	96	92
Decomposition test, oxidizing	58	76
Decomposition test, reducing	72	85

Batches having different SiO₂ contents are compared in Table 4. The resistance to decomposition under oxidizing conditions falls drastically with Si contents (expressed as SiO₂) of less than 2.5% by weight. By contrast, the resistance to decomposition under reducing conditions remains substantially constant under the selected conditions. The exact stabilizing mechanisms for SiO₂-which are important to stability under oxidizing conditions-and for MgO-which are important to stability under reducing conditions-are known. As the SiO₂ content increases, both the TEC and the Young's modulus increase, thus leading to a deterioration in thermal shock resistance. It is for this reason that the upper limit for the SiO₂ content is 5% by weight.

TABLE IV

Resistance to decomposition, modulus of elasticity and thermal expansion coefficient (TEC)
for samples having different SiO₂ contents

	10	*	*	12
Example	()
Cat. % Mg in the tialite lattice	comparison) 3		11	(comparison)
Cat. % Fe in the tialite lattice	0.6	0.6	0.6	0.6
Raw materials	0.07	0.14	0.18	0.23
	Al ₂ O ₃ , TiO ₂	Al ₂ O ₃ , TiO ₂	Al ₂ O ₃ , TiO ₂	Al ₂ O ₃ , TiO ₂
	Kaolin (Fe)	Kaolin (Fe)	Kaolin (Fe)	Kaolin (Fe)
	MgTiO ₃	MgTiO ₃	MgTiO ₃	MgTiO ₃
Chemical composition				
[% by weight]				
Al ₂ O ₃	56.06	57.02	57.61	58.14
TiO ₂	41.71	39.14	37.60	36.17
SiO ₂	1.86	3.48	4.45	5.35
MgO	0.38	0.36	0.35	0.33
Fe ₂ O ₃	0.09	0.16	0.20	0.24
	5 h/1440o			
Sintering conditions	C.	5 h/1440o C.	5 h/1440o C.	5 h/1440o C.
Al ₂ TiO ₅ content [% by				

weight]				
Sintered	99	92	85	85
Decomposition test - oxidizing	65	76	81	81
Decomposition test - reducing	94	85	86	76
Modulus of elasticity [GPa]	9	20	24	27.5
TEC [RT - 1000o C.] [10< - 6 > 1/K]	0.75	1.9	2.55	2.9

The preceding batches were calculated under the assumptions that only two crystalline phases, aluminium titanate ($\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$) and mullite ($3 \text{ Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$), are formed and that Mg and Fe dissolve completely in the aluminium titanate lattice i.e. form a solid solution. Under the conditions mentioned, the batches also reacted almost completely, so that less than 5% by weight of unreacted residual oxides ($\text{Al}_2\text{O}_3 + \text{TiO}_2$) were present under carefully controlled process conditions. The residual oxide content is usually less than 2.5% by weight. If excess aluminium oxide is additionally added, Table V, the decomposition process is distinctly accelerated.

TABLE V
Resistance to decomposition for samples with different
Al₂O₃ excesses

Example	3	13	14
Cat. % Mg in the tialite lattice	0.6	0.6	0.6
Cat. % Fe in the tialite lattice	0.14	0.14	0.14
Al ₂ O ₃ excess [% by vol.] calculated	0	1.5	5
Raw materials	Al ₂ O ₃ , TiO ₂ Kaolin (Fe) MgTiO ₃	Al ₂ O ₃ , TiO ₂ Kaolin (Fe) MgTiO ₃	Al ₂ O ₃ , TiO ₂ Kaolin (Fe) MgTiO ₃
Chemical composi- tion [% by weight]			
Al ₂ O ₃	57.02	57.73	59.37
TiO ₂	39.14	38.49	37.00
SiO ₂	3.48	3.42	3.29
MgO	0.36	0.36	0.34
Fe ₂ O ₃	0.16	0.16	0.15
Sintering conditions	5 h/1440o C.	5 h/1440o C.	5 h/1440o C.
Al ₂ TiO ₅ content [% by weight]			
Sintered	92	88	90
Decomposition test, oxidizing	76	47	6
Decomposition test, reducing	85	69	25

The following properties were measured on the batches of Examples 3 and 4:

TABLE VI
Properties of Examples 3 and 4

		Example 3	Example 4
Density (g/cm ³)	*	3.26	3.34
4-Point flexural strength (MPa)	*	48	50
static Young's modulus (GPa)	*	20	21
TEC (RT - 1000° C.) (10 ⁻⁶ - 1/K)	*	1.9	2.0
Phase composition (% by weight) measured by diffraction in fired state			
	Al ₂ TiO ₅ /mullite	92/9	90/9
	Al ₂ O ₃ /TiO ₂	0/0	0/0
after decomposition	Al ₂ TiO ₅ /mullite	76/8	78/11
test under oxidizing conditions	Al ₂ O ₃ /TiO ₂	7/4	4/3
after decomposition	Al ₂ TiO ₅ /mullite	85/8	91/9
test under reducing conditions	Al ₂ O ₃ /TiO ₂	1,5/0,5	0/0

In one particularly preferred procedure, the raw materials (for formulation, see "Examples") were suspended together with water (30% by weight) and a commercially available dispersant, ground in an attritor and the slip obtained was conventionally spray-dried. After redispersion in water and homogenization for 1 to 3 hours in a ball mill, a slip is obtained with no further additions and is processed by the method described in the Examples.

CLAIMS: What is claimed is:

[*1] 1. Sintered ceramic body which comprise doped aluminum titanate and mullite having the composition:

50-61.5% by weight Al₂O₃,

36-47.5% by weight titanium oxide, expressed as TiO₂,

2.5-5% by weight SiO₂,

with the sum total of the three components adding up to 100%, and which further comprise 0.3 to 1% by weight MgO, 0.015 to 0.5% by weight iron oxide, expressed as Fe₂O₃ and up to 1% by weight impurities.

[*2] 2. Sintered ceramic body as claimed in claim 1 wherein the MgO content is 0.3 to 0.6% by weight.

[*3] 3. Sintered ceramic body as claimed in claim 1 wherein the iron oxide content, expressed as Fe_2O_3 , is 0.05 to 0.4% by weight.

[*4] 4. Sintered ceramic body as claimed in claim 1 wherein the percentage by weight ratio of MgO to Fe_2O_3 is between 20 and 2.

[*5] 5. Sintered ceramic body as claimed in claim 2 wherein the iron oxide content, expressed as Fe_2O_3 , is 0.05 to 0.4% by weight.

[*6] 6. Sintered ceramic body as claimed in claim 2 wherein the percentage by weight ratio of MgO to Fe_2O_3 is between 20 and 2.

[*7] 7. Sintered ceramic body as claimed in claim 1, wherein the sum total of the contents of unreacted Al_2O_3 and TiO_2 after sintering is 5% or lower, by weight.

[*8] 8. Sintered ceramic body as claimed in claim 1, wherein the sum total of the contents of unreacted Al_2O_3 and TiO_2 after sintering is $\leq 2.5\%$ by weight.

[*9] 9. A process for the production of sintered ceramic body which comprises the steps of mixing, shaping and sintering a composition comprising the following components:

50-61.5% by weight Al_2O_3 ,

36-47.5% by weight titanium oxide, expressed as TiO_2 ,

2.5-5% by weight SiO_2 ,

with the sum total of the three components adding up to 100%, and which further comprise 0.3 to 1% by weight MgO , 0.015 to 0.5% by weight iron oxide, expressed as Fe_2O_3 and up to 1% by weight impurities wherein the sintering of the ceramic body at temperatures of 1250° to 1600° C. over a holding time of 0.5 to 100 hours.

[*10] 10. A process according to claim 9 wherein the sintering temperature is 1300° to 1450° C. over a holding time of 1 to 50 hours.

[*11] 11. A process according to claim 9 wherein as a first step the components are predispersed individually or in admixture by wet grinding and the mixture of wet-ground components is subsequently processed by granulation drying.

[*12] 12. A process according to claim 9 wherein the sintered ceramic body is reaction-sintered.

[*13] 13. A process according to claim 9 wherein magnesium compounds are introduced into the composition as magnesium titanates, selected from the group consisting of Mg_2TiO_4 , MgTiO_3 , MgTi_2O_5 , and mixtures thereof.

[*14] 14. A process according to claim 9 wherein iron compounds are introduced into the composition in the form of finely dispersed $\alpha\text{-Fe}_2\text{O}_3$ powder, in the form of iron-containing layer silicates, or in the form of

iron-containing kaolin.

[*15] 15. A process accordingly to claim 9 wherein iron compounds are introduced into the composition in the form of iron containing clays.

1ST PATENT of Level 1 printed in FULL format.

5,422,324

<=2> GET 1st DRAWING SHEET OF 1

Jun. 6, 1995

Aluminum titanate ceramic and process for producing the same

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CL: 501;

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REF-CITED:

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CORE TERMS: phase, ceramic, heat, cycle, aluminum, titanate, vitreous, durability, crystalline, resistance, sintered, breaking, modulus, strain, acid, casting, grain, composition, mullite, bending, raw materials, proportion, excellent, crystal, sample, deterioration, four-point, sintering, measured, liner

ABST:

The present invention provides an aluminium titanate ceramic composed of, as main crystalline phases, 60-85% of an aluminum titanate phase, 10-25% of a rutile phase, 2-10% of a corundum phase and 2-10% of a mullite phase, wherein the amount of vitreous phase is 5% or less. The aluminum titanate ceramic is superior in both heat cycle durability and casted property.

NO-OF-CLAIMS: 3

EXMPL-CLAIM: <=11> 1

NO-OF-FIGURES: 1

NO-DRWNG-PP: 1

SUM:

BACKGROUND OF THE ART AND RELATED ART STATEMENT

The present invention relates to an aluminum titanate ceramic and a process for producing said aluminum titanate ceramic. More particularly, the present invention relates to an aluminum titanate ceramic used in, for example, a head port liner, an exhaust manifold liner (these liners are for the heat insulation of the inside of an engine exhaust pipe) and a catalytic converter, as well as to a process for producing said aluminum titanate ceramic.

A ceramic using aluminum titanate as a base material has a low thermal expansion coefficient and a small Young's modulus. Hence, it is suitable for use in various members used under severe conditions in which the members are

required to have high thermal shock resistance and low thermal expansion, for example, a head port liner, an exhaust manifold liner (these liners are for the heat insulation of the inside of a gasoline engine exhaust pipe) and a catalytic converter.

It is known that in ordinary aluminum titanate (aluminum titanate is hereinafter referred to as AT) ceramic materials, the Young's modulus and the strength are generally proportional to each other. That is, as the strength is higher, the Young's modulus is larger. Conversely, as the strength is lower, the Young's modulus is smaller. This is because when an AT ceramic material has a low strength, the crystal grains of the AT ceramic material are generally large and a number of cracks exist between the grain boundaries, allowing the AT ceramic material to be easily deflected and lowering its strength. Many of conventional AT ceramic materials have a Young's modulus of about 2,000 kgf/mm² or more and a bending strength of 2-5 kgf/mm² .

Various improvements have been made for AT ceramic materials, depending upon their applications, by, for example, appropriately selecting the composition or adding appropriate additives. Japanese Patent Publication No. 5544/1985 , for example, proposes a silicate-containing aluminum titanate ceramic material made of raw materials comprising 50-60% by weight of Al₂O₃, 40-45% by weight of TiO₂, 2-5% by weight of kaolin and 0.1-1% by weight of magnesium silicate.

Japanese Patent Application Kokai (Laid-Open) No. 21756/1987 proposes an aluminum titanate-mullite ceramic material having the following composition:

MgO: 0.8 or less

Al₂O₃: 53-74%

TiO₂: 14-33%

Fe₂O₃: 1.2-5%

SiO₂: 6-20%

CaO + Na₂O + K₂O: 0.3% or less

wherein the amount of vitreous phase in the mullite matrix of ceramic is 5% or less when measured on a section of ceramic.

Japanese Patent Application Kokai (Laid-Open) No. 164760/1989 proposes a shaped sintered material composed basically of aluminum titanate, which is produced from mixed raw materials consisting of 46% by weight or more of TiO₂, 49.5% by weight or less of Al₂O₃, 3-5% by weight of SiO₂ and 0.2% by weight or less of impurities, the weight ratio of Al₂O₃ and TiO₂ being 1:0.95 to 1:1.05.

The ceramic proposed in Japanese Patent Publication No. 5544/1985 has a low Young's modulus and excellent casting property when used as a material to be cast by metal, but has the following problems. That is, the ceramic contains a magnesium silicate vitreous phase; when the ceramic is used in a heat cycle wherein high-temperature heating and cooling are repeated, the vitreous phase present at the grain boundaries moves during high temperatures; consequently, the grain boundary strength is reduced, cracks are developed at the grain boundaries, and there occurs deterioration in strength; thus, the ceramic has

poor heat cycle durability. Further, the ceramic has low acid resistance owing to the presence of said vitreous phase.

The ceramic proposed in Japanese Patent Application Kokai (Laid-Open) No. 21756/1987 has excellent heat cycle durability and is useful as a material for use in a head port liner, etc. However, the ceramic, when containing mullite in a large amount, has a high Young's modulus and shows an inferior casting property, when used as a material to be cast by metal.

The ceramic proposed in Japanese Patent Application Kokai (Laid-Open) No. 16470/1989 has excellent heat cycle durability and acid resistance but, containing TiO_2 in a large amount and consequently showing, when polished, a structure free from cracks, has a high Young's modulus and an inferior casting property.

SUMMARY OF THE INVENTION

The present invention is intended to solve the above-mentioned problems of conventional AT ceramic materials and provide an AT ceramic material having excellent heat cycle durability and a superior casting property.

According to the present invention, there is provided an aluminum titanate ceramic comprising, as main crystalline phases, 60-85% of an aluminum titanate phase, 10-25% of a futile phase, 2-10% of a corundum phase and 2-10% of a mullite phase, wherein the amount of vitreous phase is 5% or less.

According to the present invention, there is further provided a process for producing the aluminum titanate ceramic mentioned above, which comprises subjecting a mixed raw material powder consisting of 51.7-56.5% by weight of Al_2O_3 , 40.2-45.0% by weight of TiO_2 , 2.0-5.0% by weight of SiO_2 , 0.04% by weight or less of MgO and 0.1% by weight or less of a total of alkali metal and alkaline earth metal components consisting of CaO , Na_2O and K_2O to shaping, drying and sintering.

The aluminum titanate ceramic of the present invention has the above composition and comprises, as crystalline phases, not only an aluminum titanate phase but also a futile phase, a corundum phase and a mullite phase, wherein the amount of vitreous phase is controlled so as not to exceed 5% by weight; thereby, the present ceramic has excellent heat cycle durability and a superior casting property.

The reasons for excellent heat cycle durability and superior casting property are presumed to be as follows.

Firstly, conventional aluminum titanate ceramics of the Al_2O_3 - TiO_2 - SiO_2 type are generally produced by using natural minerals, etc. as raw materials, for example, clay, etc. as a SiO_2 source; as a result, most of the conventional AT ceramic materials contain a vitreous phase in an amount more than required, owing to the presence of small amounts of impurities in said clay, etc. and, when used in, for example, a head port liner, are corroded by exhaust gas from the engine and show poor durability. Meanwhile, the AT ceramic of the present invention has excellent acid resistance and high durability because it contains a very small amount of vitreous phase.

Secondly, in the AT ceramic of the present invention, since the MgO content

in raw materials is 0.04% by weight or less, the growth of AT crystal grains is suppressed and the size of AT crystal grains in the AT ceramic is small; the amount of vitreous phase in AT ceramic is very small; as a result, the grain boundary strength is very high. Meanwhile, the crystal grains of futile, corundum and mullite contained in the present AT ceramic have higher strengths than the AT crystal grains; hence, the residual stress generated owing to the anisotropy of AT crystal grains is accumulated and stored in a large amount in the AT ceramic. This residual stress in storage is released at once upon generation of any crack; and cracks are generated in the lengthwise direction of each AT crystal grain. Cracks, however, are not generated along the grain boundaries; therefore, the cracks contribute to a superior casting property but do not grow during heat cycle.

DRWDESC:

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows a relation between deflection and load in four-point bending strength test (JIS R 1601), of a ceramic sample.

DETDESC:

DETAILED DESCRIPTION OF THE INVENTION

The present invention is hereinafter described in more detail.

In the AT ceramic of the present invention, the basic components constituting the ceramic are three components, i.e., Al_2O_3 , TiO_2 and SiO_2 . The main crystalline phases consist basically of four phases, i.e., 60-85% of an aluminum titanate (Al_2TiO_5) phase, 10-25% of a rutile (TiO_2) phase, 2-10% of a corundum (Al_2O_3) phase and 2-10% of a mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) phase. The vitreous phase is controlled so as not to exceed 5%. Part of the aluminum titanate phase may contain a solid solution of aluminum titanate.

When the proportions of the crystalline phases are outside the above ranges, the resulting AT ceramic has poor heat cycle durability and an inferior casting property, making it difficult to obtain a desired AT ceramic. Particularly when the amount of vitreous phase is more than 5%, the resulting AT ceramic is low not only in acid resistance and heat cycle durability but also in the casting property.

In the present invention, the proportion of each crystalline phase is determined by the method described later.

The composition of the present AT ceramic consists of, when expressed in oxides, 51.7-56.5% by weight of Al_2O_3 , 40.2-45.0% by weight of TiO_2 , 2.0-5.0% by weight of SiO_2 , 0.4% by weight or less of MgO and 0.1% by weight or less of a total of alkali metal and alkaline earth metal components consisting of CaO , Na_2O and K_2O . This composition is substantially the same as that of the raw materials and can be obtained by preparing each raw material so as to fall in the above range. When each component of the AT ceramic is outside the above range, it is impossible to obtain an AT ceramic satisfactory in both casting property and heat cycle durability. In the AT ceramic of the present invention, the content of Fe_2O_3 is preferably 1.0% by weight or less. When Fe_2O_3 is contained in a large amount, the resulting AT ceramic has a high Young's modulus

and low casting property.

The source (raw material) of each oxide component is described. As the source for Al_2O_3 , there can be used, for example, alpha -alumina, calcined bauxite, aluminum sulfate, aluminum chloride and aluminum hydroxide. As the source for TiO_2 , there can be used, for example, rutile and anatase. As the source for SiO_2 , there can be used, for example, silica glass, kaolin, mullite and quartz.

In the raw materials for the present AT ceramic, the MgO content and the total content of alkali metal and alkaline earth metal components (CaO , Na_2O and K_2O) are selected so as to be 0.04% by weight or less and 0.1% by weight or less, respectively. The Fe_2O_3 content is selected so as to be 0.1% by weight or less. It is preferable to use alpha -alumina, in particular, low-sodium alpha -alumina as the Al_2O_3 source, rutile type titania as the TiO_2 source and kaolin as the SiO_2 source.

In the present invention, the raw materials each of a fine powdery state are mixed in the above composition, and the mixture is shaped in a desired form and sintered according to known methods to obtain an AT ceramic. In this case, each of the raw materials preferably has an average particle diameter of about 5 μm or less. When the average particle diameters of the raw materials are larger than 5 μm , the reactivity between the raw materials is low, making it difficult to obtain desired crystals. Preferably, the particle diameters of the raw materials are selected so that the AT crystal grains of the AT ceramic obtained have an average particle diameter of 4 μm or less. When the AT crystal grains are large, cracks are generated along the grain boundaries rather than in the lengthwise direction of each grain.

As the method for shaping, there can be used any known shaping method such as hot pressing, cast molding, rubber pressing or the like. The temperature for sintering can be similar to the temperature employed for sintering of ordinary ceramics, but is preferably 1,350-1,450°C. This temperature range is necessary to keep the proportions of the rutile crystalline phase and the corundum crystalline phase in their respective ranges mentioned above. In the shaping and sintering, there may be appropriately added a shaping aid, a deflocculant, a sintering aid, etc.

The present AT ceramic obtained as above, preferably has a breaking strain of 3×10^{-3} or more. When the breaking strain is less than 3×10^{-3} , the resulting AT ceramic has low casting property. The present AT ceramic preferably has a four-point bending strength of 3.0 kgf/mm^2 or more. When the four-point bending strength is less than 3.0 kgf/mm^2 , the resulting AT ceramic has poor heat cycle durability.

The present invention is hereinafter described specifically by way of Examples. However, the present invention is not restricted by these Examples.

In the present Examples, proportions of crystalline phases, amount of vitreous phase, Young's modulus, breaking strain, heat cycle durability and acid resistance were measured in accordance with the following test methods.

(1) Proportions of crystalline phases

An AT ceramic was subjected to X-ray diffraction analyses and measured for

the integral intensities I AT , I Ru , I Mu and I Co of the AT phase, futile phase (hereinafter referred to as Ru phase), mullite phase (hereinafter referred to as Mu phase) and corundum phase (hereinafter referred to as Co phase). Then, the proportion of each crystalline phase was calculated using the following formula: AT phase (%) = [I AT /I] x 100

$$\text{Ru phase (\%)} = [\text{I Ru} / \text{I}] \times 100$$

$$\text{Mu phase (\%)} = [[\text{I Mu} / 0.95] / \text{I}] \times 100$$

$$\text{Co phase (\%)} = [[\text{I Co} / 0.75] / \text{I}] \times 100$$

$$\text{wherein } I = I \text{ At} + I \text{ Ru} + I \text{ Mu} / 0.95 + I \text{ Co} / 0.75$$

TABLE 1

Crystalline phase	Test method	d (A)	Peak used	Intensity ratio
			2 theta (o)	
AT phase	ASTM 26-40	3.356	26.6	100
Ru phase	ASTM 4-0551	3.245	27.5	100
Mu phase	ASTM 15-776	3.428	26.0	95
Co phase	ASTM 10-173	3.479	25.6	75

(2) Amount of vitreous phase

One of the conventional AT materials had polygonal portions surrounded by mullite crystals, in the mullite matrix. These portions, when subjected to chemical analysis, showed a composition approximately consisting of 68% of SiO₂, 24% of Al₂O₃, 4.4% of TiO₂, 1.0% of CaO and 2.0% of KNaO. The composition is substantially the same as that of vitreous phase.

In the present invention, these polygonal portions were taken as a vitreous phase in mullite matrix. Accordingly, the vitreous phase in the present invention is a value obtained by, in the scanning electron micrograph taken for polished section of sintered AT ceramic, excluding the areas of pores and AT crystalline phase, then measuring, on the remaining area, the mullite matrix portion (MuS) and the vitreous phase portion (GS) using a planimeter, and making a calculation using the following formula.

$$\text{Vitreous phase (\%)} = [\text{GS} / \text{MuS}] \times 100$$

(3) Young's modulus

Was measured using the three-point bending and deflection angle of JIS R 1602. In this case, the load was varied from 0 to 150 gf.

(4) Breaking strain

Was measured according to the same test method as that used for measurement of the four-point bending strength of ceramics, specified by JIS R 1601. That is, for a sample having a thickness "t" (mm), the deflection shown by the sample during a period from the start of load application to the destruction of the sample was taken, in FIG. 1 showing a from a point 1 (start of load application)

to a point 4 (an intersection between a base line 3 and a perpendicular drawn from a destruction point 2 to the base line 3; then, the breaking strain of the sample was calculated from "a" and "t" using the following formula. Breaking strain = $6t \times a/1000$

Incidentally, this breaking strain is a quotient when bending strength is divided by Young's modulus determined from the deflection at the destruction point. A larger breaking strain gives superior casting property.

(5) Heat cycle durability

A sample specified by JIS R 1601 was heated for 20 minutes in a furnace of 900°C., then taken out and cooled by air flow for 10 minutes. This heat cycle procedure was repeated 600 times. The sample was measured for four-point bending strengths σ_0 (before heat cycle) and σ_1 (after heat cycle) by JIS R 1601.

From the thus obtained σ_0 and σ_1 , the heat cycle strength deterioration (%) of the sample was calculated using the following formula.

$$\text{Heat cycle strength deterioration (\%)} = [(\sigma_1 - \sigma_0) / \sigma_0] \times 100$$

(6) Acid resistance

Five same AT ceramic samples each having a square plate shape [10 mm x 10 mm x 3 mm (thickness)] were prepared and measured for respective weights (m_0). Then, they were dipped in 100 ml of a 10% aqueous hydrogen chloride solution and allowed to stand for 24 hours at 90°C., using a hot water bath. Thereafter, they were taken out, washed, dried and measured for respective weights (m_1). The acid resistance of each sample was calculated from the m_0 and m_1 , using the following formula.

$$\text{Acid resistance (\%)} = [(m_0 - m_1) / m_0] \times 100$$

The average of the acid resistances of the five samples was taken as the acid resistance of the AT ceramic tested.

EXAMPLES 1-6

There were weighed, as raw materials, fine powders of low-sodium alpha-alumina having an average particle diameter of 1.8 μm , rutile type titania having an average particle diameter of 0.2 μm and high-purity kaolin having an average particle diameter of 3 μm , so as to give a composition shown in Table 2 or 3. The three powders were uniformly mixed. To the mixture was added 1.5% by weight of a binder. The resulting mixture was subjected to further mixing and vacuum degassing. The thus obtained mixture was cast-molded in a gypsum mold to obtain a shaped material.

The shaped material was subjected to normal-pressure sintering at a temperature shown in Table 2 or 3, to obtain a sintered AT material.

The sintered AT material was measured for proportions of crystalline phases, amount of vitreous phase, Young's modulus, breaking strain, heat cycle durability, and acid resistance. The results are shown in Tables 2 and 3.

TABLE 2

	Example			
	1	2	3	4
Composition (% by weight)	*	*	*	
Al ₂ O ₃	54.2	51.7	56.5	53.0
TiO ₂	42.5	45.0	40.2	42.0
SiO ₂	3.3	3.3	3.3	5
Fe ₂ O ₃	< 0.05	< 0.05	< 0.05	< 0.05
MgO	< 0.04	< 0.04	< 0.04	< 0.04
CaO + Na ₂ O + K ₂ O	< 0.05	< 0.05	< 0.05	< 0.05
Proportions of crystalline phases (%)				
AT phase	78	70	80	60
Ru phase	15	18	10	25
Mu phase	5	10	2	5
Co phase	2	2	8	10
Vitreous phase	< 1	< 1	< 1	< 1
Sintering temperature (°C.)	1400	1375	1425	1350
Four-point bending strength (kgf/mm ²)				
	4.0	4.2	4.4	5.0
Young's modulus (%)	1900	2100	2000	2500
Breaking strain (× 10 ⁻³)	3.3	3.1	3.2	3.0
Heat cycle strength deterioration (%)	- 1	0	- 2	0
Acid resistance (%)	0.2	0.3	0.2	0.3

TABLE 3

	Example	
	5	6
Composition (% by weight)	*	
Al ₂ O ₃	55.0	54.0
TiO ₂	43.0	42.0
SiO ₂	2	3
Fe ₂ O ₃	< 0.05	1
MgO	< 0.04	0.04
CaO + Na ₂ O + K ₂ O	< 0.05	0.1
Proportions of crystalline phases (%)		
AT phase	85	75
Ru phase	11	15
Mu phase	2	3
Co phase	2	2
Vitreous phase	< 1	5
Sintering temperature (°C.)	1450	1400
Four-point bending strength (kgf/mm ²)	3.0	4.8
Young's modulus (%)	1500	2300
Breaking strain (× 10 ⁻³)	3.5	3.0
Heat cycle strength deterioration (%)	- 3	2
Acid resistance (%)	0.2	0.5

EXAMPLES 1-7

Fine powders of raw materials were weighed so as to give a composition shown in Table 4 or 5. Using the fine powders, a sintered AT material was obtained in the same manner as in Example 1. Incidentally, the sintered AT material of Comparative Example 1 was obtained in the same procedure as described in Japanese Patent Publication No. 5544/1985 mentioned above; the sintered AT material of Comparative Example 2 was obtained in the same procedure as described in Japanese Patent Application Kokai (Laid-Open) No. 21756/1987 mentioned above; and the sintered AT material of Comparative Example 3 was obtained in the same procedure as described in Japanese Patent Application Kokai (Laid-Open) No. 164760/1989 mentioned above.

Each of the sintered AT materials was measured for proportions of crystalline phases, amount of vitreous phase, Young's modulus, breaking strain, heat cycle durability and acid resistance. The results are shown in Tables 4 and 5.

TABLE 4

	Comparative Example			
	1	2	3	4
Composition (% by weight)	*	*	*	
Al ₂ O ₃	53.0	62.8	49.0	54.2
TiO ₂	43.5	21.8	47.0	42.3
SiO ₂	2.8	12.5	4	3.3
Fe ₂ O ₃	< 0.05	2.4	< 0.05	< 0.05
MgO	0.2	0.3	< 0.05	< 0.04
CaO + Na ₂ O + K ₂ O	0.5	0.19	< 0.05	< 0.05
Proportions of crystalline phases (%)				
AT phase	76	69	68	95
Ru phase	10	0	18	0
Mu phase	0	31	13	5
Co phase	4	0	1	0
Vitreous phase	10	< 1	< 1	< 1
Sintering temperature (°C.)	1400	1600	1430	1500
Four-point bending strength (kgf/mm ²)	3.2	4.1	3.9	2.2
Young's modulus (%)	1300	2900	2800	1100
Breaking strain (× 10 ⁻³)	4.0	2.2	2.0	4.2
Heat cycle strength deterioration (%)	26	- 1	0	33
Acid resistance (%)	7.6	1.2	0.3	0.3

TABLE 5

	Comparative Example		
	5	6	7
Composition (% by weight)	*	*	
Al ₂ O ₃	54.2	54.0	53.0
TiO ₂	42.3	42.3	42.0
SiO ₂	3.3	3.0	3

Fe ₂ O ₃	< 0.05	< 0.05	2.5
MgO	< 0.04	< 0.04	< 0.05
CaO + Na ₂ O + K ₂ O	< 0.05	0.5	< 0.05
Proportions of crystalline phases (%)			
AT phase	50	77	80
Ru phase	27	10	13
Mu phase	5	2	5
Co phase	18	2	2
Vitreous phase	< 1	9	< 0
Sintering temperature (°C.)	1300	1400	1400
Four-point bending strength (kgf/mm ²)	6.6	3.6	5.1
Young's modulus (%)	3100	1800	3100
Breaking strain (× 10 ⁻³)	2.6	3.2	2.4
Heat cycle strength deterioration (%)	- 2	30	2
Acid resistance (%)	0.2	6.4	0.4

As is clear from the above Examples and Comparative Examples, the sintered AT materials of the present invention are equivalent or superior to conventional sintered AT materials (Comparative Examples), in breaking strain. Also in heat cycle strength deterioration, most of the sintered AT materials of the present invention are equivalent or superior to conventional sintered AT materials.

The sintered AT material of Comparative Example 1 has a large breaking strain but shows a large heat cycle strength deterioration and a high acid resistance, i.e. poor durability. The sintered AT materials of Comparative Examples 2 and 3 each have an excellent heat cycle strength deterioration and an excellent acid resistance but shows a small breaking strain. Thus, none of the conventional sintered AT materials tested are excellent in both casting property and heat cycle durability.

In contrast, the sintered AT materials of the present invention are excellent in casting property and heat cycle durability.

The present aluminum titanate ceramic has superior casting property and high heat cycle durability, and is suitably used as a material to be casting by metal, for example, a head port liner in gasoline engine, and also as an engine head port material. Thus, it has an industrial utility.

CLAIMS: What is claimed is:

[*1] 1. An aluminum titanate ceramic consisting essentially of, on a basis of oxides, 51.7% to 56.5% by weight of Al₂O₃, 40.2% to 45.0% by weight of TiO₂, 2.0% to 5.0% by weight of SiO₂, an amount of MgO not exceeding 0.04% by weight, an amount of Fe₂O₃ not exceeding 1.0% by weight, and a total amount of CaO, Na₂O, and K₂O not exceeding 0.1% by weight, said ceramic being sintered at a temperature in a range from about 1350° C. to about 1450° C., said ceramic having a crystalline phase comprised of 60% to 85% of an aluminum titanate phase, 10% to 25% of a rutile phase, 2% to 10% of a corundum phase, and 2% to 10% of a mullite phase, and said ceramic further having 5% or less of a vitreous

phase.

[*2] 2. The aluminum titanate ceramic of claim 1, wherein a portion of said aluminum titanate phase contains a solid solution of aluminum titanate.

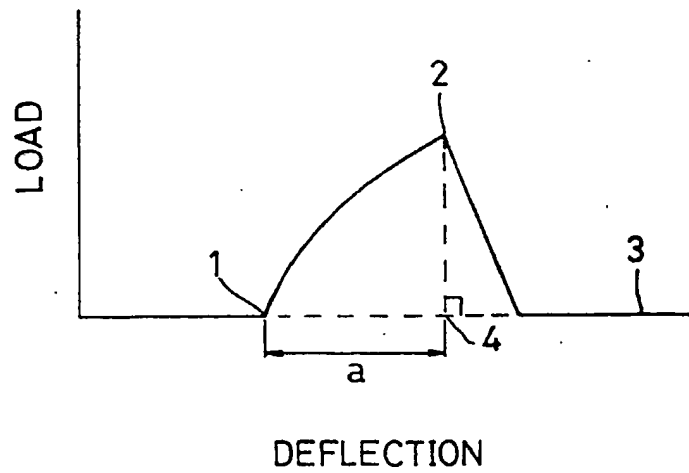
[*3] 3. The aluminum titanate ceramic of claim 1, wherein said ceramic has a breaking strain of 3×10^{-3} or more and a four-point bending strength of at least 3.0 kgf/mm² .

U.S. Patent

June 6, 1995

5,422,324

FIG. 1



25TH PATENT of Level 1 printed in FULL format.

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Multicellular monolithic ceramic body and preparation
thereof

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SEARCH-FLD: 106#73.33, 40R, 73.2; 252#477R; 264#56, 177R, 63; 501#134

REF-CITED:

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CORE TERMS: ceramic, honeycomb, aluminum, titanate, thermal, composition, coefficient, porosity, gas, multicellular, monolithic, plastic, fired, compressive, firing, resistance, additive, frontal, incorporation, sintering, catalyst, oxide, thin, refractory, powder, clay, decomposition, extruding, extrusion, cordierite

ABST:

A multicellular monolithic ceramic body having many gas passages partitioned

by thin walls is made of aluminum titanate as a major constituent and has less than 0.15% of a thermal expansion coefficient at 1000° C. and higher than 350 kg./cm² of a compressive strength as zero of an open frontal area as the properties in the direction along the gas passages and more than 35% of a porosity.

NO-OF-CLAIMS: 20

EXMPL-CLAIM: <=7> 1

NO-OF-FIGURES: 0

NO-DRAWING-PP: 0

SUM:

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a novel, useful multicellular monolithic ceramic body which is referred to as a ceramic honeycomb and a preparation thereof.

2. Description of the Prior Art

Discharge gas of internal combustion engines such as automotive emission contain noxious components such as carbon monoxide and hydrocarbons. The gas causes air pollution together with discharge gases from the other industrial apparatuses. In view of prevention of public pollution, it is necessary to convert the noxious components into non-noxious components. It has been considered that a catalyst device is one of the most effective devices.

As a catalyst for cleaning the automotive emission etc., it has been proposed to use a pellet or grain type catalyst or a multicellular monolithic catalyst having many gas passages partitioned by thin walls in one or two direction. The latter, multicellular monolithic ceramic body has remarkable advantages of low pressure loss of the emission gas, high wearing resistance under severe vibration and light weight and compact and has the improved durability. Therefore, the demand has been increased. However, the multicellular monolithic ceramic body has not enough thermal shock resistance in comparison with the pellets in view of the structure. Therefore, it is necessary to form it by a refractory ceramic having low thermal expansion and contraction and low expansion coefficient as the material. This fact is one of serious problem for using such ceramic honeycombs in this application.

As materials for the ceramic honeycombs, it has been proposed to use alumina-silica, alumina, zirconia-alumina, zirconia-magnesia, mullite, zirconia-silica (zircon), zircon-mullite, titania, magnesia-alumina spinel, zirconia and the other special non-oxide type ceramics such as Si₃N₄ and carbon. However, it has not been practically used except the following magnesia-alumina-silica (2MgO.2Al₂O₃.5SiO₂:cordierite),

lithia-alumina-silica ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$; $n:2-8$, beta -spodumene), because of high thermal expansion coefficient and the oxidative consumption at high temperature. It has been highly required to improve the catalyst in view of severe condition in applications. There is substantially not any hope for the improvement.

The cordierite has been widely used because of low expansion (thermal expansion coefficient of 0.12 to 0.3% at 1000° C.) and relatively high stability at high temperature (low decomposition) as the characteristics of ceramics.

The above-mentioned beta -spodumene has the thermal expansion coefficient (- 0.1 to - 0.2% at 1000° C.) lower than that of cordierite. The temperature for the allowable application is too low as lower than 1200° C. In the practical condition requiring higher heat resistance, beta -spondumene has not been practically used. In feature, there is substantially not possibility to use it.

The cordierite honeycombs have been practically used, however, they have certain disadvantages.

One is the requirement of higher heat resistance, because of improvement of engines, and instantaneous high temperature (caused by back-fire etc.) and long durability. The other is the requirement to large thermal shock resistance.

On the other hand, the following physical characteristics are required for the fabricated product as the ceramic honeycomb as a carrier for a catalyst. That is, high porosity is required for carrying the catalyst and high strength of the substrate is required because of the requirement of thinner walls of the ceramic honeycomb for effectively using the expensive catalyst. It is not easy to satisfy both characteristics in view of the balance that higher porosity results in lower strength. The problem has not been dissolved.

It has been studied to overcome all or most of the disadvantages of the conventional products and to develop an improved ceramic honeycomb and has been succeeded to develop a satisfactory ceramic honeycomb.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a novel, useful ceramic honeycomb having characteristics of high heat resistance, high porosity, high compressive strength and low thermal expansion coefficient which are suitable for cleaning the automotive emission and have not been attained.

The foregoing and other objects of the present invention have been attained by providing a multicellular monolithic ceramic body having many gas passages partitioned by thin walls which is made of aluminum titanate as a major constituent and has less than 0.15% of a thermal expansion coefficient at 1000° C. and higher than 350 kg./cm² of a compressive strength as zero of an open frontal area as the properties in the direction along the gas passages and more than 35% of a porosity.

The multicellular monolithic ceramic body can be prepared by fabricating a specific ceramic plastic composition by extruding it through a die.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The multicellular monolithic ceramic body as the ceramic honeycomb and the applications will be illustrated in detail.

In the specification, the honeycomb means a fired body having honeycomb structure having many gas passages partitioned by thin walls. The cross-sectional shape of the gas passage perpendicular to the direction of the gas flow is not limited to hexagonal and can be octagonal, quadrilateral, trigonal or circular shape etc. The open frontal part, the size of the gas passage and the thickness of the thin wall will be described below.

The ceramic honeycomb of the present invention has been developed to be optimum as a catalyst carrier for cleaning automotive emission from the above-mentioned viewpoint. Thus, it can be also used for cleaning discharge gases from the other industrial apparatuses and for the other usages beside the catalyst carrier, for example, carriers for heat exchange, burner tile, radiation walls, heaters, thermal reactors, filters, heat insulators and orifices for hot fluid.

The chemical composition of the fired ceramic of the multicellular monolithic ceramic body as the ceramic honeycomb of the present invention is made of aluminum titanate ($\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$) as the major component to have the specific characteristics of the substrate.

The required characteristics of the substrate are not easily given. Aluminum titanate selected as the substrate of the present invention should be also considered in view of the required characteristics. For example, the thermal expansion coefficient of the aluminum titanate is decreased depending upon the increase of degree of the firing. The thermal expansion coefficient and the strength are inferior when the substrate has high porosity and low degree of the firing.

In the present invention, this problem is dissolved by the selection of aluminum titanate and the incorporation of SiO_2 component and the extrusion molding method.

It has been known that a desired strength of aluminum titanate is not imparted without sintering and the incorporation of SiO_2 component is effective for the sintering, however, it has not been considered to prepare a ceramic honeycomb by using aluminum titanate and to incorporation of the SiO_2 component for producing a product which can be practically used. Aluminum titanate has not been considered as a material for practical uses because of unstable at high temperature. In the present invention, it has been succeeded to provide a ceramic honeycomb having the above-mentioned characteristics by the incorporation of the SiO_2 component.

The amount of the SiO_2 component for the ceramic honeycomb of the present invention is preferably in a range of 4 to 10 wt. % especially 5 to 8 wt. % as the chemical composition of the fired ceramic honeycomb. When the amount of the SiO_2 component is not enough, the strength is inferior whereas when it is too much, the thermal expansion coefficient is too high. The characteristics of the ceramic honeycomb can be imparted in said range.

The physical characteristics of the ceramic honeycomb of the present invention will be described later in detail.

Now, the preparation of the ceramic honeycomb having such characteristics especially the desired preparation with the incorporation of the SiO_2 component

will be described.

The desired process of the present invention is to prepare the multicellular monolithic ceramic body as the ceramic honeycomb by fabricating a multicellular monolithic body having many gas passages partitioned by thin walls in an extruding direction by extruding a ceramic plastic composition comprising aluminum titanate or an aluminum titanate precursor as a major constituent through a die for extruding in a form of the multicellular body; calcining the resulting fabricated composition to obtain said multicellular monolithic ceramic body made of aluminum titanate as a major constituent of the ceramic composition and having characteristics of less than 0.15% of a thermal expansion coefficient at 1000° C. and more than 350 kg./cm² of a compressive strength as zero of an open frontal area as the characteristics in the direction of extrusion and more than 35% of a porosity.

The ceramic plastic composition is a mixture of refractory materials comprising a synthesized aluminum titanate or an aluminum titanate precursor which is convertible to aluminum titanate by firing after fabricating to the honeycomb, as the major constituent and is an extrudable composition for extruding through a die for extrusion molding. In order to impart such extrudable fluidity as plastic property, it is possible to use a viscosity regulator of an organic macromolecular compound such as methylcellulose and starch or a mixture of clay and water. It is also possible to use a composition of a resin such as polystyrene or polyethylene or a mixture of two or more resins which is used for an injection molding.

The incorporation of clay is desirable in view of higher strength of the ceramic honeycomb.

In order to decrease the thermal expansion coefficient of the fired ceramic honeycomb, it is indispensable to impart certain sintering for the ceramic plastic composition with certain firing contraction. In order to obtain the sintered product having a porosity of about 35 to 45% and low thermal expansion coefficient and high strength it is necessary to incorporate a porosity increasing additive (to form pores by firing).

As the sintering additive, the SiO₂ component for imparting high strength is incorporated in the ceramic plastic composition. It is optimum to incorporate clay in view of the plastic property. It is also possible to incorporate the other oxides such as Fe₂O₃, Cr₂O₃ and SnO₂ which are also effective for reducing the decomposition of aluminum titanate at high temperature. It is usually effective to incorporate Y₂O₃, La₂O₃ or CeO₂ at a ratio of about 0.5 to 5 wt. % based on aluminum titanate.

The thermal expansion coefficient of aluminum titanate is reduced depending upon the increase of the degree of sintering. The product having high porosity and low sintered state has high thermal expansion coefficient and low strength. It has been found that the incorporation of Y₂O₃, La₂O₃ or CeO₂ component with the SiO₂ component in the composition is effective to overcome the problem.

These components can be used as the sintering additive and also as the high temperature stabilizer for reducing decomposition of aluminum titanate at high temperature and as the component for increasing strength at high temperature, with synergistic effect with the SiO₂ component.

It is advantageous to incorporate all of the sintering additive in the synthesis of aluminum titanate though it is possible to add to the ceramic plastic composition for fabricating the honeycomb as the incorporation of the SiO₂ component.

The sintering additive is usually incorporated in a form of an oxide. It is possible to incorporate it in a form of a precursor which is converted to the oxide by firing.

The sintering additive will be further illustrated. It is optimum to use La₂O₃ which imparts excellent effect for strength of the fired product with the SiO₂ component and also imparts synergistic effect for the stability at high temperature with the SiO₂ component. The pure aluminum titanate honeycomb has fatal defect in view of the stability at high temperature and accordingly it could not be considered to use it in an industrial purpose. That is, Al₂O₃.TiO₂ is decomposed to Al₂O₃ and TiO₂ in an oxidative atmosphere at 900° C. to 1350° C. whereby the characteristics of low thermal expansion and high strength are lost. The tendency for the decomposition is especially remarkable in a reducing atmosphere. In order to overcome these disadvantages, various studies have been made to succeed in the improvement of the stability at high temperature with low thermal expansion of the aluminum titanate honeycomb by the incorporation of the SiO₂ component and the La₂O₃ component. The same effect can be imparted by using Y₂O₃ or CeO₂ instead of La₂O₃. The mixture thereof can be also used.

The optimum amount of the specific additive is in a range of 0.5 to 2 wt. % in the fired composition. When it is less than 0.5 wt. %, the effect is not enough whereas it is unnecessary to incorporate more than 2 wt. % of the specific additive. The amount of the specific additive can be decreased by the incorporation of the Fe₂O₃ component. There is possibility to cause disadvantage of increase of the thermal expansion and decrease of the melting point by the incorporation of more than 2 wt. % of the specific additive.

The incorporation of the Fe₂O₃ component will be described. The incorporation of the Fe₂O₃ component is effective as the sintering additive and also effective for imparting synergistic effect as the high temperature stabilizer with SiO₂, La₂O₃, etc. in an oxidative atmosphere. On the contrary, the incorporation of the Fe₂O₃ component results in acceleration of the decomposition in the reducing atmosphere. Therefore, it is effective depending upon the condition. The amount of the Fe₂O₃ component in such condition is preferably more than 0.4 wt. % to give a total amount of Fe₂O₃, La₂O₃, CeO₂ and Y₂O₃ of 0.9 to 5 wt. %.

When the Fe₂O₃ component is not incorporated (especially in the use of the product in the reducing atmosphere), it is possible to incorporate more than 2 wt. % of La₂O₃, CeO₂ or Y₂O₃ component. When it is more than 5 wt. %, the cost increases without any improvement of the characteristics. Sometimes it causes to increase the thermal expansion.

The porosity increasing additive can be incorporated in the ceramic plastic composition. A binder such as methylcellulose and polystyrene; and coke powder, and also cellulose powder can be used as the porosity increasing additive.

The sintering additive and the porosity increasing additive can be added in the synthesis of aluminum titanate. The thermal decomposition inhibitor is preferably incorporated in the synthesis of aluminum titanate.

The refractory material as the major constituent of the ceramic plastic composition will be illustrated. Alumina (Al_2O_3) source and titania (TiO_2) source for the formation of aluminum titanate are used. It is preferable to incorporate the synthesized aluminum titanate as all or most of the major constituent of the ceramic plastic composition.

The synthesis of aluminum titanate will be illustrated. The aluminum titanate is produced by preparing a mixture of the alumina source, the titania source the sintering additive, the thermal decomposition inhibitor and a binder and fabricating it and firing it. It is optimum to use aluminum hydroxide which is converted to alumina by firing as the alumina source. The use of aluminum hydroxide is advantageous in view of the cost, the purity and the easy synthesis and also the preparation of the ceramic honeycomb having excellent physical characteristics.

As a titania source, anatase type synthesized TiO_2 is usual used, though rutile type TiO_2 can be used.

The molar ratio of Al_2O_3 to TiO_2 is preferably in a range of 1.00:1.00 to 0.80:1.20 as the theoretical composition. When, the content of Al_2O_3 is more than the range, the sintering is not easily resulted and the thermal expansion coefficient is too high and the stability at high temperature is inferior whereas when the content of TiO_2 is more than the range, the thermal expansion coefficient is too high. The desired stability at high temperature is given in said range.

It is necessary to incorporate the SiO_2 component for sintering the aluminum titanate which is obtained from the sources or synthesized. When the amount of the SiO_2 component and the method of the incorporation are considered as described, the effect of the invention is especially advantageous.

The amount of the SiO_2 component in the fired ceramic honeycomb is preferably in a range of 4 to 10 wt. %. A part of the SiO_2 component as 10 to 60% is preferably incorporated in the sources for the synthesis of the aluminum titanate used as the refractory material in the ceramic plastic composition.

The SiO_2 component is usually incorporated for 10 to 60% of the total SiO_2 component in the synthesis of the aluminum titanate and for 90 to 40% in the preparation of the ceramic plastic composition whereby the ceramic honeycomb having excellent characteristics can be effectively attained. Moreover, it has been found to impart the optimum effect for the strength of the fired product.

When a firing temperature for producing the aluminum titanate clinker is too high, the thermal expansion coefficient of the fired ceramic honeycomb is increased though the thermal expansion coefficient of the clinker is not affected. When it is too low, the aluminum titanate is not satisfactorily produced. It is preferably in a range of 1450° to 1600° C. especially 1500° to 1550° C.

The resulting aluminum titanate clinker is preferably used by pulverizing to be fine powder as the refractory source. In the present invention, it is preferable to use it in a form of powder having more than 80% of fine powder passing through 300 mesh sieve. When it is the fine powder, it is advantageous in the stable extrusion molding for a honeycomb having thin walls (for example,

0.15 to 0.2 mm).

The ceramic plastic composition is fed into the conventional extruding machine to fabricate the composition into the honeycomb shape. The ratio of the refractory source in the ceramic plastic composition is preferably to give more than 85 wt. % of aluminum titanate component and 4 to 10 wt. % of SiO₂ component and less than 10 wt. % preferably less than 6 wt. % of the other components as the chemical composition of the fired ceramic honeycomb.

As the ratio of the refractory source in the ceramic plastic composition, it is preferable to give 85 to 95 wt. % of the synthesized aluminum titanate, 15 to 5 wt. % of clay especially 90 to 95 wt. % of the former and 10 and 5 wt. % of the latter.

The extrusion machine can be a die disclosed in U.S. Pat. No. 3,038,201 and Japanese Unexamined Patent Publication No. 42386/1972 or can be the conventional extrusion machine. The honeycomb obtained by extrusion-molding by such extrusion machine has low thermal expansion coefficient in the direction of the extrusion and has high thermal shock resistance.

The shapes of the ceramic honeycomb can be considered depending upon the applications. In the application for the automotive emission control, it is usual to form many gas passages having cross-sectional view of square or other desired shape as disclosed in U.S. Pat. No. 3,899,326, No. 3,853,485, and No. 3,983,283.

The honeycomb fabricated by the extrusion machine is dried and fired. The temperature for firing is in a range of 1350° to 1500° C. preferably 1380° to 1450° C. When the temperature is too high, the porosity required for the ceramic honeycomb used for the catalyst carrier is decreased. When the temperature is too low, the thermal expansion coefficient is not decreased.

In accordance with the process of the present invention, the fired ceramic honeycomb made of aluminum titanate having excellent characteristics for honeycomb which could not be previously provided. The physical characteristics will be illustrated.

The ceramic honeycomb comprises more than 85 wt. % of aluminum titanate component to have the melting point higher than that of the conventional cordierite honeycomb, whereby it is durable in the continuous use at higher than 1400° C. and it is durable at about 1650° C. for a short time. This is superior to the safety temperature of the cordierite honeycomb of up to 1300° C.

The thermal expansion coefficient in the direction of the gas passages can be less than 0.15% at 1000° C. This is similar to the minimum thermal expansion coefficient of the cordierite honeycomb of 0.12%. It is possible to give less than 0.1% or less than 0.09% of the thermal expansion coefficient if desired. These characteristics are enough to be durable to severe repeated uses as the automotive emission control honeycomb.

At the characteristics of the fired ceramic honeycomb the ceramic honeycomb made of the aluminum titanate of the present invention has more than 35% of a porosity which is enough to carry a catalyst together with more than 350 kg./cm² of a compressive strength (as zero of an open frontal area in the gas

flow direction) as the special characteristics of high heat resistance and high thermal shock resistance superior to those of the cordierite honeycomb. It has been difficult to impart both characteristics.

When the porosity is too high, it is natural to decrease the strength lower than the required level. It is preferable to be up to 45% of the porosity except an improvement for holding by an automobile to be capable of low strength or an application which does not require high strength.

The structure of the ceramic honeycomb having many gas passages partitioned by thin walls which has the above-mentioned characteristics can be the following ranges.

A thickness of the thin wall is in a range of 0.08 to 0.5 mm; a density of holes as the gas passages of 40 to 200 per 1 cm² and an open frontal area (perpendicular to the gas flow direction) of 50 to 85%.

These characteristics are not inferior to the characteristics of the conventional honeycombs whose strength is lower in the use at 800o to 1000o C. whereas the ceramic honeycomb of the present invention made of aluminum titanate has the strength at such temperature higher than the strength at room temperature. The high temperature and thermal spalling durability in the use of the ceramic honeycomb of the present invention is remarkably higher than the durability of the cordierite honeycomb.

In accordance with the present invention, the ceramic honeycomb having excellent characteristics of high heat resistance, high porosity, high compressive strength and low thermal expansion, which are important for a ceramic honeycomb for catalyst carrier but could not be given by the conventional technology. The practical value of the ceramic honeycomb is remarkable.

DETDISC:

The present invention will be further illustrated by certain examples and references which are provided for purposes of illustration only and are not intended to be limiting the present invention.

EXAMPLE 1

Aluminum hydroxide synthesized anatase TiO₂, clay, ferric oxide, yttrium oxide, methylcellulose and water were mixed and kneaded and molded in a form of rough rod having a diameter of 60 mm. The molded composition was dried and fired at 1550o C. for 5 hours to obtain a synthetic aluminum titanate clinker comprising 3 wt. % of SiO₂, 2 wt. % of Fe₂O₃, 1 wt. % of Y₂O₃ and the remainder of Al₂O₃.TiO₂. The synthetic clinker was pulverized to pass through 300 mesh sieve to use it as the synthetic aluminum titanate (referring to as Aluminum titanate source I).

100 Wt. parts of the refractory source of 92 wt. % of the Aluminum titanate source I and 8 wt. % of clay was admixed with 10 wt. parts cellulose powder, and 5 wt. parts of methylcellulose and water to prepare a ceramic plastic composition. The composition was extruded through a die for honeycomb extrusion molding to form a honeycomb having many gas passages having square cross sectional view which are partitioned by thin walls.

The molded composition was fired at the maximum temperature of 1400o C. to

obtain the ceramic honeycomb having the following properties.

Composition of ceramic honeycomb

Al₂O₃.TiO₂ of 89.0 wt. %

SiO₂ of 6.5 wt. %

Fe₂O₃ of 2.0 wt. %

Y₂O₃ of 1.0 wt. %

the others of 0.5 wt. %

Characteristics

Porosity of 38%

Thermal expansion coefficient of 0.08% (extruding direction at 1000° C.)

Compressive strength of 445 kg./cm² >(extruding direction) (120 kg./cm² >in an open frontal area of 73%)

Heat resistance (*Note 1) of higher than 1600° C.

Thermal shock resistance (*Note 2) of higher than 900° C.

n *Note 1: A regular hexahedron honeycomb having each side of 2 cm was kept in a furnace at a specific temperature for three minutes and the temperature for no deformation was measured. n *Note 2: The temperature of a furnace was elevated each 100° C. to flush heat the sample at a specific temperature and an operation for 1 cycle of heating in furnace pair of opposing arrows cooling in air was repeated for three times to carry out the thermal spalling test for temperature difference. The temperature for no damage was measured.

Structure of ceramic honeycomb

Thickness of wall of 0.15 mm

Density of holes as gas passages of 95/cm² >

Open frontal area of 73%.

It is understood that the ceramic honeycomb having such characteristics can be practically used as a catalyst carrier for automotive emission control, in view of the following characteristics of the typical cordierite honeycomb which is commercialized and practically used.

Porosity of 32%

Thermal expansion coefficient of 0.18% (1000° C.)

Compressive strength of 450 kg./cm² >(121 kg./cm² >in an open frontal area of 73%)

Heat resistance (See Note 1) of lower than 1400° C.

Thermal shock resistance (See Note 2) of lower than 600o C.

EXAMPLE 2

In the preparation of Aluminum titanate source I in Example 1, excess of clay was incorporated to give 6.5 wt. % of SiO₂ component. This is referred to as Aluminum titanate source Ia.

100 Wt. parts of Aluminum titanate source Ia was admixed with 5 wt. parts of methylcellulose, 10 wt. parts of cellulose powder and water without any clay to prepare a ceramic plastic composition. In accordance with the process of Example 1 except using the ceramic plastic composition, a fired ceramic honeycomb was prepared.

The resulting ceramic honeycomb had similar characteristics to those of Example 1 except having relatively lower compressive strength of about 350 kg./cm². This product can be used for certain purposes though the condition for the application is limited.

EXAMPLE 3

In accordance with the process of Example 1 except using 10 wt. parts of polystyrene and 5 wt. parts of polyethylene instead of methylcellulose without water, to prepare a ceramic plastic composition and a honeycomb was extruded at 160o C. and dipped in methylenechloride for 15 minutes after cooling to remove polystyrene, a ceramic honeycomb was obtained by firing it. The characteristics of the product are as follows.

Porosity of 36%

Thermal expansion coefficient of 0.07% (extruding direction at 1000o C.)

Compressive strength of 400 kg./cm² >(extending strength: 108 kg./cm² >in an open frontal area of 73%)

Heat resistance of higher than 1600o C.

Thermal shock resistance of higher than 900o C.

REFERENCE 1

In accordance with the process of Example 1 except that excess of clay was incorporated in Aluminum titanate source Ia ceramic honeycomb having 12 wt. % of SiO₂ component was prepared by firing the ceramic plastic composition. The ceramic honeycomb had a thermal expansion coefficient of 0.22% at 1000o C. which is out of the range of the present invention. In the shock test at high temperature described in Note 1, several cracks were formed to fall apart.

REFERENCE 2

In the preparation of Aluminum titanate source I, SiO₂ component was not incorporated to prepare Aluminum titanate source Ib.

In accordance with the process of Example 1 except using Aluminum titanate source Ib to prepare the ceramic plastic composition, a fired ceramic honeycomb

containing 3 wt. % of SiO₂ component was obtained.

The ceramic honeycomb had a desired thermal expansion of 0.05% at 1000° C. but low compressive strength of about 150 kg./cm² which is out of the range of the present invention.

REFERENCE 3

In accordance with the process of Example 1 except firing a molded honeycomb composition at 1320° C., a ceramic honeycomb was prepared. The ceramic honeycomb had a porosity of about 45% but had fluctuated strengths and thermal expansion coefficient of a half of the products were about 0.20% at 1,000° C. The firing at this temperature is not preferable.

EXAMPLE 4

In accordance with the process of Example 1 except using alumina powder (alpha -Al₂O₃ crystal grains of about 3 μ) was used instead of aluminum hydroxide, a fired ceramic honeycomb was obtained.

The ceramic honeycomb had a porosity of 40%, a thermal expansion coefficient of 0.14% (at 1000° C.) and a compressive strength of 380 kg./cm² (102 kg./cm² at an open frontal area of 73%).

EXAMPLE 5

60 Wt. parts of Aluminum titanate source I of Example 1 was admixed with 29 wt. parts of a mixture of alumina and anatase type titania powder (which form aluminum titanate in firing after the molding of the honeycomb), and 10 wt. parts of clay, 0.7 wt. parts of ferric oxide, and 0.3 wt. parts of Y₂O₃. 100 Wt. parts of the mixture was admixed with cellulose powder, methylcellulose and water and the mixture was kneaded to prepare a ceramic plastic composition. In accordance with the process of Example 1, a ceramic honeycomb was prepared from the composition.

The resulting ceramic honeycomb had a porosity of 36%, a thermal expansion efficiency of 0.13% (at 1000° C.) and a compressive strength of 450 kg./cm² (122 kg./cm² at an open frontal area of 73%).

REFERENCE 4

In accordance with the process of Example 1 except firing the composition for Aluminum titanate source at 1650° C., a ceramic honeycomb was prepared. The ceramic honeycomb had a porosity of 40%, a compressive strength of 370 kg./cm² (100 kg./cm² in an open frontal area of 73%), but had large thermal expansion coefficient of 0.25% (at 1000° C.) which is out of the range of the present invention.

EXAMPLE 6

In accordance with the process of Example 1 except that 1.5 wt. % of La₂O₃ was used instead of Y₂O₃, a fired ceramic honeycomb was prepared.

The ceramic honeycomb had a porosity of 37%, a thermal expansion coefficient of 0.05% (at 1000° C.) and a compressive strength of 460 kg./cm² (125 kg./cm² in an open frontal area of 73%).

EXAMPLE 7

In accordance with the process of Example 1 except that 1.0 wt. % of CeO₂ was

used instead of Y_2O_3 , a fired ceramic honeycomb was prepared.

The ceramic honeycomb had a porosity of 41%, a thermal expansion coefficient of 0.13% (at 1000° C.) a compressive strength of 370 kg./cm² >(90 kg./cm² >in an open frontal area of 73%).

EXAMPLE 8

In accordance with the process of Example 1 except that ferric oxide was not used to prepare Aluminum titanate source Ic and 100 wt. parts of a refractory material comprising 90 wt. % of Aluminum titanate source I' and 10 wt. % of clay was used, a fired ceramic honeycomb was prepared. The ceramic honeycomb had a higher porosity of 43% but lower compressive strength of 390 kg./cm² >and the similar other characteristics.

The high temperature stability of the ceramic honeycomb was superior to that of Example 1 in an oxidative atmosphere but was slightly inferior to that of Example 1 in a reducing atmosphere. These are acceptable in the practical uses.

The product was heated at 1000° C. in an atmosphere of 1% of CO and 99% of N₂ for 10 hours and the heat-treatment was repeated for 5 times.

According to X-ray analysis, a decomposition of aluminum titanate for about 3% was found in the case of Example 1 whereas no decomposition was found and no adverse effect to the appearance and the thermal expansion coefficient was found in the case of Example 8.

The product was heated at 1000° C. in air for 1000 hours.

No decomposition was found in the case of Example 8 whereas a decomposition of aluminum titanate for about 4% was found in the case of Example 1.

CLAIMS: We claim:

[*1] 1. A multicellular monolithic ceramic body having many gas passages partitioned by thin walls, consisting essentially of: aluminum titanate as the major constituent and from 4 to 10 wt. % SiO₂, said ceramic body having a thermal expansion coefficient less than 0.15% at 1000° C., a compressive strength greater than 350 kg/cm² >as taken along the direction of the gas passages based only on the solid surface of said body and not including open areas of said body and a porosity of greater than 35%.

[*2] 2. The multicellular monolithic ceramic body of claim 1, wherein said porosity is less than 45%.

[*3] 3. The multicellular monolithic ceramic body of claim 1, wherein said thermal expansion coefficient is less than 0.1.

[*4] 4. The multicellular monolithic ceramic body of claim 1, wherein said ceramic consists essentially of more than 85 wt. % of aluminum titanate component in the chemical composition.

[*5] 5. The multicellular monolithic ceramic body of claim 1, wherein said ceramic consists essentially of 5 to 8 wt. % of SiO₂ component.

[*6] 6. The multicellular monolithic ceramic body of claims 1, 2, 3, 4 or 5, wherein the thickness of said thin walls partitioning said gas passages of the fired body is in the range of 0.08 to 0.5 mm, the frequency of the holes as the gas passages numbers from 40 to 200 per cm^2 and the open frontal area of the ceramic ranges from 50 to 85%.

[*7] 7. The multicellular monolithic ceramic body of claims 1, 2, 3, 4 or 5, wherein the molar ratio of Al_2O_3 to TiO_2 as the components of aluminum titanate is in a range of 1.00:1.00 to 0.8:1.2.

[*8] 8. The multicellular monolithic ceramic body of claim 1, wherein the chemical composition of said fired body consists essentially of more than 80 wt. % of aluminum titanate, 4 to 10 wt. % of SiO_2 and 0.5 to 5 wt. % of at least one oxide selected from the group consisting of La_2O_3 , CeO_2 and Y_2O_3 .

[*9] 9. The multicellular monolithic ceramic body of claim 8, wherein the chemical composition of said fired body further consists essentially of more than 0.4 wt. % of Fe_2O_3 and 0.9 to 5 wt. % of at least one oxide selected from the group consisting of La_2O_3 , CeO_2 and Y_2O_3 including Fe_2O_3 .

[*10] 10. The multicellular monolithic ceramic body of claim 8 or 9, wherein the chemical composition consists essentially of more than 85 wt. % of aluminum titanate and 4 to 10 wt. % of SiO_2 .

[*11] 11. The multicellular monolithic ceramic body of claim 10, which further consists essentially of 0.5 to 2 wt. % of at least one of La_2O_3 , CeO_2 and Y_2O_3 .

[*12] 12. A process for preparing a multicellular monolithic ceramic body having many gas passages therein, partitioned by thin walls, comprising:

(a) extruding a plastic ceramic composition comprising aluminum titanate or an aluminum titanate precursor as the principal constituent and from 4% to 10% by wt. of SiO_2 based on the metal oxide components of the composition through an extruding die; and

(b) calcining the extruded mass at a temperature of 1350° to 1500° C., thereby obtaining said ceramic body having a thermal expansion coefficient less than 0.15% at 1000° C., a compressive strength greater than 350 kg/cm^2 as taken along the direction of the gas passages based only on the solid surface of said body and not including open areas of said body and a porosity of greater than 35%.

[*13] 13. The process according to claim 12, wherein said ceramic is based upon 85% to 95% by wt. aluminum titanate.

[*14] 14. The process of claim 12, wherein the refractory materials of said plastic ceramic composition consist essentially of from 85 to 95 wt. % of aluminum titanate, 15 to 5 wt. % of clay and less than 10 wt. % of the other components.

[*15] 15. The process of claim 14, wherein said refractory materials contain from 0.5 to 5 wt. % of at least one metal oxide selected from the group consisting of La_2O_3 , CeO_2 and Y_2O_3 .

[*16] 16. The process of claim 15, wherein said refractory materials further consist essentially of more than 0.4 wt. % of Fe_2O_3 component and 0.9 to 5 wt. % of at least one metal oxide selected from the group consisting of La_2O_3 , CeO_2 and Y_2O_3 components including Fe_2O_3 among the lanthanum oxide materials.

[*17] 17. The process of claim 12, wherein the aluminum titanate contains 10 to 60 wt. % of SiO_2 based on the total SiO_2 components in the fired ceramic body.

[*18] 18. The process of claim 12, wherein the aluminum titanate comprises more than 80% of fine powder passing through 300 mesh.

[*19] 19. The process of claim 18, wherein the aluminum titanate is produced by firing a mixture of a source of alumina and a source of titania as major constituents at 1450° to 1600° C.

[*20] 20. The process of claim 19, wherein the alumina source is aluminum hydroxide.

4TH PATENT of Level 1 printed in FULL format.

5,346,870

<=2> GET 1st DRAWING SHEET OF 4

Sep. 13, 1994

Aluminum titanate ceramic and process for producing the same

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SEARCH-FLD: 501#73, 112, 118, 119, 126, 127, 134, 136, 5, 128; 264#56

REF-CITED:

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CORE TERMS: titanate, aluminum, phase, mullite, crystalline, cycle, heat, ceramic, sintered, rutile, rare earth, particle, alumina, glass, magnesite, strain, alpha, breaking, durability, powder, raw material, composition, sintering, crystal, oxide, earth, bending, casting, grain, fine

ABST:

An aluminum titanate ceramic has as main crystalline phases, a crystalline phase of aluminum titanate and a solid solution thereof, a crystalline phase of mullite and a crystalline phase of rare earth titanate represented by RE₂Ti₂O₇ (RE represents Y, Yb, Er, Dy, Ho, Tm or Lu). The aluminum titanate ceramic is superior in casting property and has high heat cycle durability.

NO-OF-CLAIMS: 5

EXMPL-CLAIM: <=9> 1

NO-OF-FIGURES: 4

NO-DRWNG-PP: 4

SUM:

BACKGROUND OF THE INVENTION AND RELATED ART STATEMENT

The present invention relates to an aluminum titanate ceramic and a process for producing said aluminum titanate ceramic. More particularly, the present invention relates to an aluminum titanate ceramic used in, for example, a head port liner, an exhaust manifold liner (these liners are for the heat insulation of the inside of an engine exhaust pipe) and a catalytic converter, as well as

to a process for producing said aluminum titanate ceramic.

A ceramic using aluminum titanate as a base material has a low thermal expansion coefficient and a small Young's modulus. Hence, it is suitable for use in various members used under severe conditions in which the members are required to have high thermal shock resistance and low thermal expansion, for example, in a head port liner, an exhaust manifold liner (these liners are for the heat insulation of the inside of gasoline engine exhaust pipe) and in a catalytic converter.

It is known that in ordinary aluminum titanate materials (aluminum titanate material is hereinafter referred to as AT material), the Young's modulus and the strength are generally proportional to each other. That is, as the strength is higher, the Young's modulus is larger. Conversely, as the strength is lower, the Young's modulus is smaller. This is because when an AT material has a low strength, the crystal grains of the AT material are generally large and a number of cracks exist between the grain boundaries, allowing the AT material to be easily deflected and lowering its strength. Many of the conventional AT materials have a Young's modulus of about 2,000 Kgf/mm² or more and a bending strength of 2-5 Kgf/mm².

Various improvements have been made for AT materials, depending upon their applications, by adding additives, etc. thereto. In this connection, it was proposed to add a rare earth oxide in order to suppress the decomposition of aluminum titanate at high temperatures and impart a high strength.

For example, Japanese Patent Publication No.3629/1982 proposes a low-thermal-expansion ceramic comprising, as a main phase, an aluminum titanate containing at least one rare earth element selected from the group consisting of Y, La and Ce. Japanese Patent Application Kokai (Laid-Open) No. 257165/1989 proposes an aluminum titanate containing a rare earth oxide, mullite and iron titanate, which is stable even at high temperatures of about 1,000o-1,300o C. Japanese Patent Application Kokai (Laid-Open) No. 258670/1990 proposes a low-thermal-expansion ceramic consisting of an aluminum titanate-magnesium titanate solid solution and Yttrium titanate, which is stable at high temperatures.

The ceramics proposed in Japanese Patent Publication No. 3629/1982 and Japanese Patent Application Kokai (Laid-Open) No. 258670/1990, contain rare earth element(s). However, they have a small number of cracks and consequently have a high strength and a high Young's modulus; when used as a casting material for metal they give low deflection and are unable to absorb the strain applied, that is, they are inferior in casting; when subjected to a heat cycle wherein high temperature heating and cooling are repeated, new cracks appear at the grain boundaries and thereby their strengths are deteriorated.

The aluminum titanate proposed in Japanese Patent Application Kokai (Laid-Open) No. 257165/1989 contains mullite and a rare earth oxide. However, it is inferior in casting similarly to the above ceramics, and further has insufficient heat cycle durability because it has cracks in the crystal grains and at the grain boundaries.

SUMMARY OF THE INVENTION

The present invention aims at providing an AT material which has eliminated

the above-mentioned drawbacks of conventional AT materials and which has superior casting property and high heat cycle durability.

According to the present invention, there is provided an aluminum titanate Ceramic comprising, as main crystalline phases, a crystalline phase of aluminum titanate and a solid solution thereof, a crystalline phase of mullite and a crystalline phase of rare earth titanate represented by $RE_2Ti_2O_7$ (RE represents Y, Yb, Er, Dy, Ho, Tm or Lu).

According to the present invention, there is further provided a process for producing an aluminum titanate which comprises preparing a plurality of raw material powders of 5 μm or less in average particle diameter, selected from the group consisting of an Al_2O_3 source, a TiO_2 source, a SiO_2 source, a Fe_2O_3 source, a MgO source, a rare earth element source, a mullite source and aluminum titanate, mixing the raw material powders to obtain a mixture, shaping the mixture to obtain a shaped body, drying the shaped body to obtain a dried body and then sintering the dried body.

The aluminum titanate ceramic of the present invention has excellent casting property and high heat cycle durability because the aluminum titanate ceramic is constituted as above and comprises, as main crystalline phases, a crystalline phase of aluminum titanate and a solid solution thereof, a crystalline phase of mullite and a crystalline phase of rare earth titanate represented by $RE_2Ti_2O_7$ (RE represents Y, Yb, Er, Dy, Ho, Tm or Lu).

The reason is not clear but is presumed to be as follows. That is, when a sintered aluminum titanate material contains mullite and a rare earth titanate therein, the rare earth titanate takes the form of a dendrite structure and exists at the boundaries between aluminum titanate crystals and mullite crystals and binds them strongly; when such a sintered aluminum titanate material is subjected to heat cycle and undergoes thermal stress, no cracks appear at the grain boundaries which are ordinarily generated at such grain boundaries, and cracks appear in the aluminum titanate crystals and the mullite crystals and these cracks contribute to the improvement of casting property; meanwhile, since the bonding between crystals is strong as mentioned above, no cracks appears at the grain boundaries during heat cycle and thereby high heat cycle durability is obtained.

In the present invention, the use of fine powder starting materials of 5 μm or less in average particle diameter enables the production of intended aluminum titanate ceramic because the use gives rise to (1) active reaction between TiO_2 and rare earth compound and (2) consequent formation of rare earth titanate of dendrite structure at grain boundaries.

The crystalline phases in the present aluminum titanate ceramic consist mainly of a crystalline phase of aluminum titanate and its solid solution, a mullite crystalline phase and a rare earth titanate crystalline phase. The aluminum titanate ceramic of the present invention may further comprise other crystalline phases of rutile, corundum, etc.

DRWDESC:

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 shows a relation between deflection and load in a four-point bending

strength test (JIS R 1601), of a ceramic sample.

FIG. 2 shows X-ray diffraction patterns of the sintered AT materials obtained in Examples and Comparative Examples.

FIG. 3 shows a scanning type electron micrograph (magnification = 800) showing the crystal structure of the sintered AT material obtained in one Example of the present invention.

FIG. 4 shows a scanning type electron micrograph (magnification = 800) showing the crystal structure of the sintered AT material obtained in one Comparative Example of the present invention.

DETDISC:

DETAILED DESCRIPTION OF THE INVENTION

The basic components constituting the aluminum titanate ceramic of the present invention are six components of Al_2O_3 , TiO_2 , $\text{SiO}_2\text{Fe}_2\text{O}_3$, MgO and RE_2O_3 , and the main crystalline phases of the present aluminum titanate ceramic consist of three phases of aluminum titanate (Al_2TiO_5), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and rare earth titanate ($\text{RE}_2\text{Ti}_2\text{O}_7$). At least part of the aluminum titanate phase is a solid solution of aluminum titanate. The RE of $\text{RE}_2\text{Ti}_2\text{O}_7$ is a rare earth element selected from Y, Yb, Er, Dy, Ho, Tm and Lu and does not refer to any other rare earth element. The rare earth elements other than Y, Yb, Er, Dy, Ho, Tm and Lu, each have large ionic radius and are unable to form a rare earth titanate, and vitrify at grain boundaries, making it impossible to obtain an intended AT material, and therefore are not used in the present invention.

That the aluminum titanate ceramic of the present invention is composed mainly of the above-mentioned three crystalline phases and one of them is a $\text{RE}_2\text{Ti}_2\text{O}_7$ crystalline phase, is clear from the X-ray diffraction patterns of the present Examples shown in FIG. 2 and the scanning type electron micrograph of the present Example shown in FIG. 3, both shown later.

The composition of the present aluminum titanate ceramic, when expressed on the basis of oxides, consists of 40-60% by weight of Al_2O_3 , 30-45% by weight of TiO_2 , 1-10% by weight of SiO_2 , 0-4% by weight of Fe_2O_3 , 0.1-1.5% by weight of MgO and 0.1-10% by weight of RE_2O_3 . When the content of each oxide component is outside the above range, it is impossible to obtain an aluminum titanate ceramic superior both in casting property and heat cycle durability. Particularly when the content of RE_2O_3 is less than 0.1% by weight, the resulting aluminum titanate ceramic has inferior heat cycle durability.

The source (raw material) of each oxide component is described. As the source for Al_2O_3 , there can be used, for example, alpha -alumina, calcined bauxite, aluminum sulfate, aluminum chloride and aluminum hydroxide. As the source for TiO_2 , there can be used, for example, rutile and anatase. As the source for SiO_2 , there can be used, for example, silica glass, kaolin, mullite and quartz. As the source for MgO there can be used, for example, magnesite, magnesium nitrate and magnesium oxide. As the source for RE_2O_3 , there can be used, for example, the oxides, chlorides, carbonates, nitrates and hydroxides of the above-mentioned rare earth elements.

As the source for Al_2TiO_5 , there can be used (A) an aluminum titanate powder obtained by wet- or dry-blending the above-mentioned Al_2O_3 source and TiO_2 source and then calcining and grinding the blend, or (B) an aluminum titanate obtained by subjecting an aluminum- and titanium-containing solution to synthesis and calcination. The Al_2TiO_5 source may contain at least one oxide selected from SiO_2 , Fe_2O_3 , MgO and RE_2O_3 .

The raw materials used in the present invention contain the above-mentioned Al_2TiO_5 source in an amount of preferably 5% by weight or more, more preferably 20% by weight or more based on all the raw materials.

In the present invention, the raw materials each in fine powdery state are mixed in the above composition, then shaped in a desired form, and sintered to obtain a low-thermal-expansion ceramic. In this case, the raw materials, particularly the TiO_2 source and Al_2TiO_5 source, preferably have an average particle diameter of about 5 μm or less. When the average particle diameters of the raw materials are larger than 5 μm , the reactivity between the raw materials is low and no rare earth titanate is precipitated, giving an aluminum titanate ceramic of inferior heat cycle durability.

As the method for shaping, there can be used any known shaping method such as hot pressing, cast molding, rubber pressing or the like. The temperature for sintering can be about 1,400-1,650°C. similarly to the temperature employed for sintering of ordinary ceramics. In the shaping and sintering, there may be appropriately added a shaping aid, a deflocculant, a sintering aid, etc.

The present invention is hereinafter described in more detail by way of Examples. However, the present invention is in no way restricted to the following Examples.

In the Examples, breaking strain and heat cycle durability were measured according to the following methods.

(1) Breaking strain

Was measured according to the same test method as that used for measurement of the four-point bending strength of ceramics, specified by JIS R 1601. That is, For a sample having a thickness "t" (mm), the deflection shown by the sample during a period from the start of load application to the destruction of the sample was taken, in FIG. 1 showing a relation between deflection and load, as a length "a" (mm) from a point 1 (start of load application) to a point 4 (an intersection between a base line 3 and a perpendicular drawn from a destruction point 2 to the base line 3; then, the breaking strain of the sample was calculated from "a" and "t" using the following formula.

$$\text{Breaking strain} = 6t.a/1000$$

Incidentally, this breaking strain is a quotient when bending strength is divided by Young's modulus determined from the deflection at destruction point. A larger breaking strain gives superior casting property,

(2) Heat cycle durability

A sample having a length of L (mm) was heated for 20 minutes in a furnace of 900°C., then taken out and cooled by air flow for 10 minutes. This heat cycle procedure was repeated 600 times. Thereafter, the length L_1 (mm) of the sample was measured.

The sample was also measured for four-point bending strengths σ_{ϕ} (before heat cycle) and σ_1 (after heat cycle) by JIS R 1601.

From the thus obtained L_{100} , L_1 , σ_{ϕ} and σ_1 , the heat cycle dimensional change (%) and heat cycle strength deterioration (%) of the sample were calculated using the following formulas.

$$\text{Heat cycle dimensional change (\%)} = [(L_1 - L_{\phi}) / L_{\phi}] \times 100$$

$$\text{Heat cycle strength deterioration (\%)} = [(\sigma_1 - \sigma_{\phi}) / \sigma_{100}] \times 100$$

EXAMPLES 1-4

The raw material fine powders shown in Table 1 were weighed so as to give a given composition. Thereto were added 22% by weight of water and 0.5% by weight of a polyacrylic acid type deflocculant. The mixture was stirred in a pot mill for 5 hours to obtain a uniform blend. To the blend was added 1.5% by weight of a binder, and the mixture was stirred and degassed under vacuum. The resulting blend was subjected to cast molding using a gypsum mold to obtain a shaped material.

The shaped material was calcined at a temperature shown in Table i under normal pressure to obtain four sintered AT materials.

The X-ray diffraction patterns of the sintered AT materials obtained in Examples 1-3 are shown in FIG. 2. As is clear from FIG. 2, there is present in each pattern the crystalline phase of a rare earth titanate oxide, i.e., $\text{Yb}_2\text{Ti}_2\text{O}_7$ in Example 1, $\text{Y}_2\text{Ti}_2\text{O}_7$ in Example 2 and $\text{Er}_2\text{Ti}_2\text{O}_7$ in Example 3.

The scanning type electron micrograph of the crystal structure of the sintered AT material obtained in FIG. 1 is shown in FIG. 3. In FIG. 3, a crystalline phase of $\text{Yb}_2\text{Ti}_2\text{O}_7$ shining in a white color is observed on the surfaces of crystal grains, which confirms the presence of a crystalline phase of rare earth titanate oxide similarly to the case of the X-ray diffraction pattern.

Each of the sintered AT materials was further measured for breaking strain and heat cycle durability. The results are shown in Table 1.

The "A" shown in Table 1 as an Al_2TiO_5 source is a sintered ground aluminum titanate powder of 5 μm or less obtained by dry-mixing an Al_2O_3 source and a TiO_2 source and subjecting the blend to calcination and sintering. The "B" shown in Table 1 also as an Al_2TiO_5 source is an aluminum titanate powder of 1 μm obtained by subjecting an aqueous solution of an Al_2O_3 source and a TiO_2 source to synthesis and calcination. Each of the raw material fine powders used had the following average particle diameter: α -alumina = about 1.7 μm , rutile = about 0.2 μm , magnesite = about 4.3 μm , silica glass = about 3 μm , mullite = about 4 μm , and each rare earth oxide = about 5 μm .

TABLE 1

Example

Pat. No. 5346870, *

	1	2	3	4
Raw materials	*	*	*	
Al ₂ O ₃ source	alpha	alpha	alpha	alpha
TiO ₂ source	-Alumina	-Alumina	-Alumina	-Alumina
Al ₂ TiO ₅ source	Rutile	Rutile	Rutile	Rutile
	A	A	A	A
SiO ₂ source	Silica	Silica	Silica	
Fe ₂ O ₃ source	glass	glass	glass	Silica glass
MgO source	-	-	-	-
Rare earth source	Magnesite	Magnesite	Magnesite	Magnesite
Mullite source	Yb ₂ O ₃	Y ₂ O ₃	Er ₂ O ₃	Dy ₂ (CO ₃) ₃
Composition (% by weight)	Mullite	Mullite	Mullite	Mullite
Al ₂ O ₃	57	57	57	57
TiO ₂	36	36	36	36
SiO ₂	6	6	6	6
Fe ₂ O ₃	0	0	0	0
MgO	0.5	0.5	0.5	0.5
RE ₂ O ₃	0.5	0.5	0.5	0.5
TiO ₂ particle size D ₅₀ (μm)	0.2	0.2	0.2	0.2
Al ₂ TiO ₅ particle size D ₅₀ (μm)	1.0	1.0	1.0	1.0
Sintering temperature (°C.)	1500	1500	1500	1500
Rare earth crystalline phase	Yb ₂ Ti ₂ O ₇	Y ₂ Ti ₂ O ₇	Er ₂ Ti ₂ O ₇	Dy ₂ Ti ₂ O ₇
Breaking strain (x 10 ⁻³)	6.0	5.4	6.0	5.3
4-Point bending strength (Kg/mm ²)	2.4	2.4	2.5	2.8
Heat cycle dimensional change (%)	0.05	0.06	0.04	0.03
Heat cycle strength deterioration (%)	- 20	- 12	- 11	- 13

EXAMPLES 5-8

The raw material fine powders shown in Table 2 were weighed so as to give a given composition and subjected to the same procedure as in Example 1 to obtain four sintered AT materials. Each of the raw material fine powders used had the same average particle diameters as in Example 1.

Each of the sintered AT materials obtained was measured for breaking strain and heat cycle durability. The results are shown in Table 2. In Table 2, the "A" and "B" shown each as an Al₂TiO₅ source are the same as in Table 1.

TABLE 2

	Example			
	5	6	7	8
Raw materials	*	*	*	
Al ₂ O ₃ source	alpha	alpha	alpha	alpha
TiO ₂ source	-Alumina	-Alumina	-Alumina	-Alumina
Al ₂ TiO ₅ source	Rutile	Rutile	Rutile	Rutile
	A	A	A	A
	Silica	Silica	Silica	

SiO ₂ source	glass	glass	glass	Silica glass
Fe ₂ O ₃ source	-	-	-	-
MgO source	Magnesite	Magnesite	Magnesite	Magnesite
Rare earth source	Ho ₂ Cl ₃	Tm(OH) ₃	Lu ₂ (NO ₃) ₃	Yb ₂ O ₃
Mullite source	Mullite	Mullite	Mullite	Mullite
Composition (% by weight)				
Al ₂ O ₃	57	57	57	57.2
TiO ₂	36	36	36	36.2
SiO ₂	6	6	6	6
Fe ₂ O ₃	0	0	0	0
MgO	0.5	0.5	0.5	0.5
RE ₂ O ₃	0.5	0.5	0.5	0.1
TiO ₂ particle size D50 (μ m)	0.2	0.2	0.2	0.2
Al ₂ TiO ₅ particle size D50 (μ m)	1.0	1.0	1.0	1.0
Sintering temperature (°C.)	1500	1500	1500	1500
Rare earth crystalline phase	Ho ₂ Ti ₂ O ₇	Tm ₂ Ti ₂ O ₇	Lu ₂ Ti ₂ O ₇	Yb ₂ Ti ₂ O ₇
Breaking strain ($\times 10^{-3}$)	5.9	5.6	5.7	6.5
4-Point bending strength (Kg/mm ²)	2.4	2.8	2.3	2.1
Heat cycle dimensional change (%)	0.10	0.11	0.04	0.24
Heat cycle strength deterioration (%)	- 10	- 15	- 12	- 4

EXAMPLES 9-12

The raw material fine powders shown in Table 3 were weighed so as to give a given composition and subjected to the same procedure as in Example 1 to obtain four sintered AT materials. Each of the raw material fine powders used had the same average particle diameters as in Example 1.

Each of the sintered AT materials obtained was measured for breaking strain and heat cycle durability. The results are shown in Table 3. In Table 3, the "A" and "B" shown each as an Al₂TiO₅ source are the same as in Table 1.

TABLE 3

	Example			
	9	10	11	12
Raw materials	*	*	*	
Al ₂ O ₃ source	alpha	alpha	Calcined	
TiO ₂ source	-Alumina	-Alumina	bauxite	-
Al ₂ TiO ₅ source	Rutile	Rutile	Anatase	Rutile
	A	A	B	B
	Silica	Silica		Silica
SiO ₂ source	glass	glass	Clay	glass
Fe ₂ O ₃ source	-	-	Red iron oxide	Ilmenite
MgO source	Magnesite	Magnesite	MgO	Magnesite
Rare earth source	Yb ₂ O ₃	Yb ₂ O ₃	YbCl ₃	Er ₂ O ₃
Mullite source	Mullite	Mullite	Kaolin	Mullite
Composition (% by weight)				
Al ₂ O ₃	56.2	52	57	50
TiO ₂	35.3	32.5	33	42

SiO ₂	6	5	8	5
Fe ₂ O ₃	0	0	1.0	2.0
MgO	0.5	0.5	-	0.5
RE ₂ O ₃	2.0	10	1.0	0.5
TiO ₂ particle size D50 (μ m)	0.2	0.2	0.4	-
Al ₂ TiO ₅ particle size D50 (μ m)	1.0	1.0	2.0	2.0
Sintering temperature (°C.)	1500	1500	1400	1500
Rare earth crystalline phase	Yb ₂ Ti ₂ O ₇	Yb ₂ Ti ₂ O ₇	Yb ₂ Ti ₂ O ₇	Er ₂ Ti ₂ O ₇
Breaking strain ($\times 10^{-3}$)	5.8	5.3	5.8	6.1
4-Point bending strength (Kg/mm ²)	2.7	3.0	2.8	3.1
Heat cycle dimensional change (%)	0.05	0.05	0.14	0.13
Heat cycle strength deterioration (%)	- 18	- 16	- 11	- 4

EXAMPLES 13-16

The raw material fine powders shown in Table 4 were weighed so as to give a given composition and subjected to the same procedure as in Example 1 to obtain four sintered AT materials. Each of the raw material fine powders used had the same average particle diameters as in Example 1.

Each of the sintered AT materials obtained was measured for breaking strain and heat cycle durability. The results are shown in Table 4. In Table 4, the "A" and "B" shown each as an Al₂TiO₅ source are the same as in Table 1.

TABLE 4

	Example			
	13	14	15	16
Raw materials	*	*	*	
	gamma			
Al ₂ O ₃ source	-Alumina	Al ₂ (SO ₄) ₃	Al(OH) ₃	AlCl ₃
TiO ₂ source	Anatase	Rutile	Rutile	Rutile
Al ₂ TiO ₅ source	B	B	B	B
		Silica	Silica	
SiO ₂ source	Quartz	glass	glass	Silica glass
Fe ₂ O ₃ source	Fe(NO ₃) ₃	Ilmenite	FeCl ₃	Fe(OH) ₃
MgO source	MgCl ₃	Mg(NO ₃) ₃	MgO	Magnesite
Rare earth source	Y(NO ₃) ₃	Er ₂ O ₃	Er ₂ O ₃	Er ₂ O ₃
	Al ₂ O ₃ +			
Mullite source	SiO ₂	Mullite	Mullite	Mullite
Composition (% by weight)				
Al ₂ O ₃	57	40	60	51
TiO ₂	30	41	30	45
SiO ₂	10	10	7	1
Fe ₂ O ₃	-	4	0	1
MgO	1.0	0.1	1.5	1
RE ₂ O ₃	2.0	4.9	1.5	1

TiO ₂ particle size D50 (μ m)	1.0	0.2	0.2	0.2
Al ₂ TiO ₅ particle size D50 (μ m)	2.0	2.0	2.0	2.0
Sintering temperature (°C.)	1600	1550	1550	1550
Rare earth crystalline phase	Y ₂ Ti ₂ O ₇	Er ₂ Ti ₂ O ₇	Er ₂ Ti ₂ O ₇	Er ₂ Ti ₂ O ₇
Breaking strain ($\times 10^{-3}$)	5.4	5.2	5.5	5.7
4-Point bending strength (Kg _f /mm ²)	3.4	2.2	2.4	1.8
Heat cycle dimensional change (%)	0.09	0.15	0.16	0.19
Heat cycle strength deterioration (%)	- 8	- 9	- 14	- 10

COMPARATIVE EXAMPLES 1-7

The raw material fine powders shown in Table 5 or 6 were weighed so as to give a given composition and subjected to the same procedure as in Example 1 to obtain sintered AT materials. Incidentally, the sintered AT material of Comparative Example 6 was obtained by the above-mentioned process described in Japanese Patent Application Kokai (Laid-Open) No. 257165/1989, and the sintered AT material of Comparative Example 7 was obtained by the above-mentioned process described in Japanese Patent Application Kokai (Laid-Open) No. 258670/1990.

The X-ray diffraction patterns of the sintered AT materials obtained in Comparative Examples 2-4 are shown in FIG. 2. As is clear from FIG. 2, when a rare earth oxide of Pr, Nd or Sm was used, no peak for crystalline phase of rare earth titanate was observed, which indicates that no crystalline phase of rare earth titanate was formed.

The scanning type electron micrograph of the crystal structure of the sintered AT material obtained in Comparative Example 2 is shown in FIG. 4. In FIG. 4, unlike the case of FIG. 3, there is no area shining in a white color and the presence of Pr₂Ti₂O₇ crystalline phase was not confirmed.

The sintered AT materials obtained were measured also for breaking strain and heat cycle durability. The results are shown in Tables 5 and 6. In Tables 5 and 6, the "A" and "B" shown each as an Al₂TiO₅ source are the same as in Table 1.

As is clear from the above Examples and Comparative Examples, the sintered AT materials of the present invention have breaking strains equivalent or superior to those of conventional sintered AT materials shown in Comparative Examples, and have very high heat cycle durabilities (strength deterioration is 0% or less and dimensional change is 0.3% or less, in all the cases).

The present aluminum titanate ceramic which is a sintered AT material, has superior casting property and high heat cycle durability, and is suitably used as a casting material for metal, for example, a head port liner in a gasoline engine, and also as an engine head port material. Thus, it has an industrial utility.

TABLE 5

	Comparative Example			
	1	2	3	4
Raw materials	*	*	*	

	alpha	alpha	alpha	alpha
Al ₂ O ₃ source	-Alumina	-Alumina	-Alumina	-Alumina
TiO ₂ source	Rutile	Rutile	Rutile	Rutile
Al ₂ TiO ₅ source	A	A	A	A
		Silica		
SiO ₂ source	Silica glass	glass	Silica glass	Silica glass
Fe ₂ O ₃ source	-	-	-	-
MgO source	Magnesite	Magnesite	Magnesite	Magnesite
Rare earth source	Ce ₂ O ₃	Pr ₆ O ₁₁	Nd ₂ O ₃	Sm ₂ Cl ₃
Mullite source	Mullite	Mullite	Mullite	Mullite
Composition (% by weight)				
Al ₂ O ₃	57	57	57	57
TiO ₂	36	36	36	36
SiO ₂	6	6	6	6
Fe ₂ O ₃	0	0	0	0
MgO	0.5	0.5	0.5	0.5
RE ₂ O ₃	0.5	0.5	0.5	0.5
TiO ₂ particle size D ₅₀ (μ m)	0.2	0.2	0.2	0.2
Al ₂ TiO ₅ particle size D ₅₀ (μ m)	1.0	1.0	1.0	1.0
Sintering temperature (°C.)	1500	1500	1500	1500
Rare earth crystalline phase	Vitreous phase	Vitreous phase	Vitreous phase	Vitreous phase
Breaking strain ($\times 10^{-3}$)	5.6	5.8	5.8	5.4
4-Point bending strength (Kg/mm ²)	2.1	2.3	2.5	2.6
Heat cycle dimensional change (%)	0.41	0.51	0.67	0.48
Heat cycle strength deterioration (%)	11	8	15	10

TABLE 6

Comparative Example

	5	6	7
Raw materials	*	*	
	alpha		alpha
Al ₂ O ₃ source	-Alumina	alpha -Alumina	-Alumina
TiO ₂ source	Rutile	Rutile	Rutile
Al ₂ TiO ₅ source	A	B	-
SiO ₂ source	Silica glass	-	-
Fe ₂ O ₃ source	-	Red iron oxide	-
MgO source	Magnesite	Silica glass	MgCO ₃
Rare earth source	-	Y(NO ₃) ₃	Y ₂ O ₃
Mullite source	Mullite	Kaolin	-
Composition (% by weight)			
Al ₂ O ₃	57.3	56	48.8
TiO ₂	36.2	20.5	47.4
SiO ₂	6	14	-

Fe2O3	0	8	-
MgO	0.5	-	2.0
RE2O3	0	1.5	1.8
TiO2 particle size D50 (μ m)	0.2	40	0.4
Al2TiO5 particle size D50 (μ m)	1.0	40	-
Sintering temperature (°C.)	1500	1500	1500
Rare earth crystalline phase	-	Y2O3	Y2Ti2O7
Breaking strain ($\times 10^{-3}$)	6.1	4.8	4.1
4-Point bending strength (Kgf/mm ²)	2.0	1.4	2.8
Heat cycle dimensional change (%)	0.72	8.5	0.63
Heat cycle strength deterioration (%)	22	54	19

CLAIMS: What is derived is:

[*1] 1. An aluminum titanate ceramic comprising:

40-60% by weight of Al₂O₃, 30-45% by weight of TiO₂, 1-10% by weight of SiO₂, 0-4% by weight of Fe₂O₃, 0.1-1.5% by weight of MgO and 0.1-10% by weight of RE₂O₃, where RE represents Y, Yb, Er, Dy, Ho, Tm or Lu;

in the form of a crystalline phase of aluminum titanate and a solid solution thereof, a crystalline phase of mullite and a crystalline phase of rare earth titanate represented by RE₂Ti₂O₇.

[*2] 2. An aluminum titanate ceramic according to claim 1, further comprising at least one crystalline phase of the ceramic selected from rutile and corundum.

[*3] 3. A process for producing an aluminum titanate which comprises preparing a plurality of raw material powders of 5 μ m or less in average particle diameter, consisting essentially of an Al₂O₃ source, a TiO₂ source, an SiO₂ source, an Fe₂O₃ source, an MgO source, a rare earth element source, a mullite source and Al₂TiO₅ source,

mixing the raw material powders to obtain a mixture,

shaping the mixture to obtain a shaped body,

drying the shaped body to obtain a dried body and then sintering the dried body to obtain an aluminum titanate ceramic comprising 40-60% by weight of Al₂O₃, 30-45% by weight of TiO₂, 1-10% by weight of SiO₂, 0-4% by weight of Fe₂O₃, 0.1-1.5% by weight of MgO and 0.1-10% by weight of RE₂O₃, where RE represents Y, Tb, Er, Dy, Ho, Tm or Lu, in the form of a crystalline phase of aluminum titanate and a solid solution thereof, a crystalline phase of mullite and a crystalline phase of rare earth titanate represented by RE₂Ti₂O₇.

[*4] 4. A process for producing an aluminum titanate according to claim 3, wherein the raw materials contain the Al₂TiO₅ source in an amount of 5% by weight or more based on all the raw materials.

[*5] 5. A process for producing an aluminum titanate according to claim 3,

wherein the raw materials contain the Al_2TiO_5 source in an amount of 20% by weight or more based on all the raw materials.

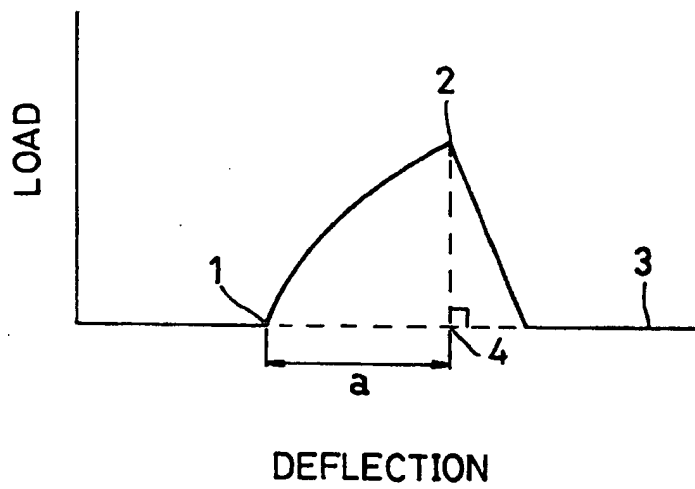
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FIG. 1



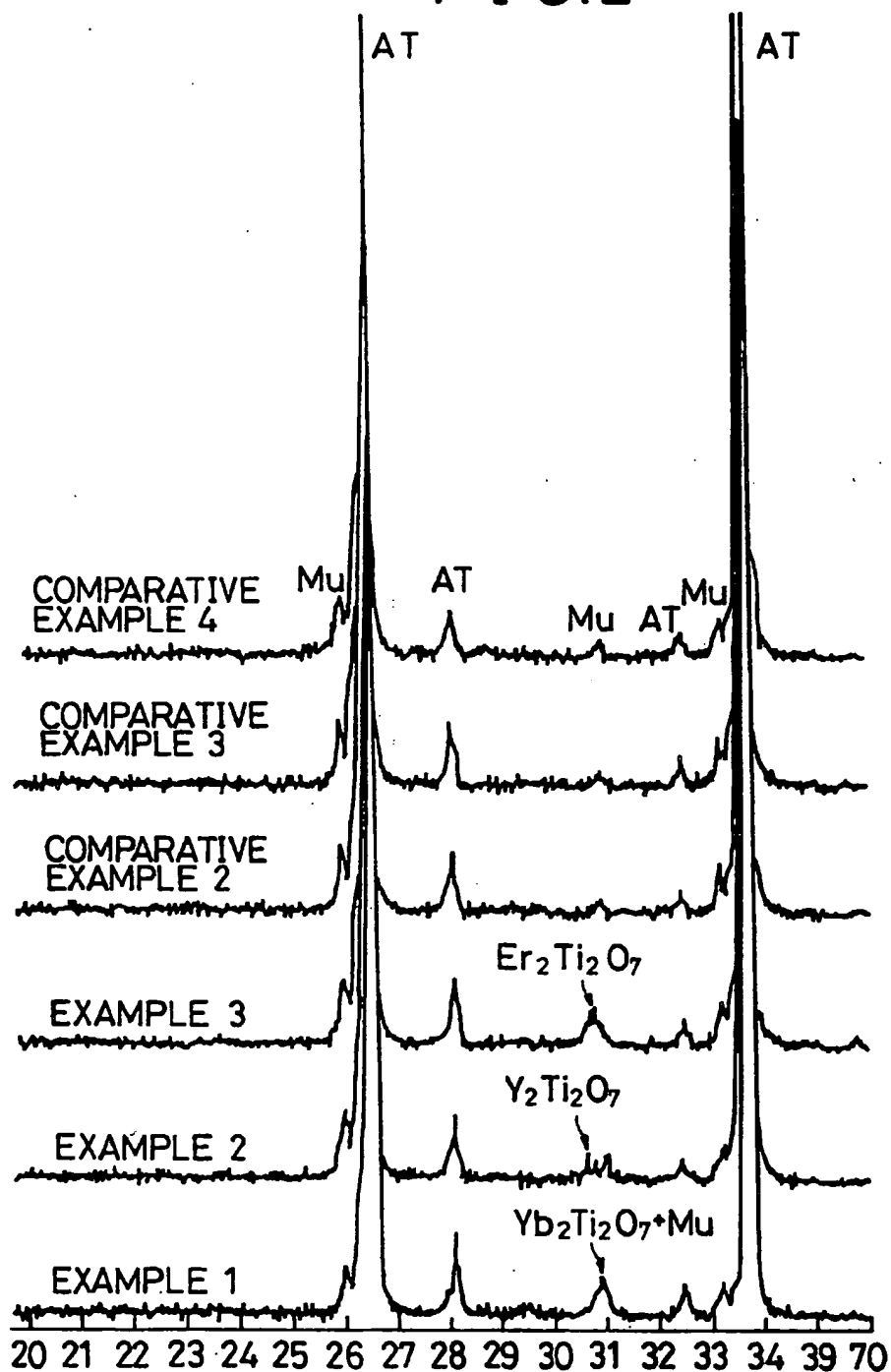
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FIG. 2



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FIG. 3



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FIG. 4

